C–H Bond activation by dicationic platinum(II) complexes

Tom G. Driver, Travis J. Williams, Jay A. Labinger,* and John E. Bercaw*

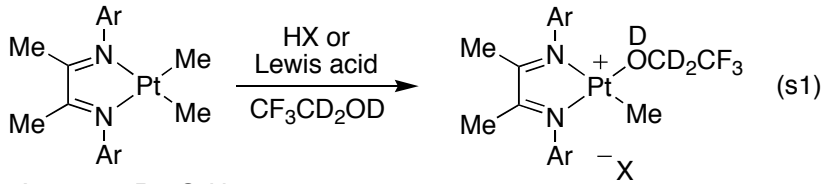
Arnold and Mabel Beckman Laboratories of Chemical Synthesis
California Institute of Technology, Pasadena, California 91125

Supporting Information

Contents:

General. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Varian 600 or 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 *Network* Mass Selective detector, and were obtained by peak matching. All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was purified by sublimation (90 °C, 0.5 mmHg). Trifluoroborane was purified following the procedure of Brown and co-workers:[1] the borane was condensed into benzonitrile and evacuated. The borane was liberated from the resultant complex by mild heating to 60 °C. The borane was passed through two –78 °C traps and condensed at –196 °C. It was then vacuum distilled by warming to –78 °C. A known volume of BF_3 was then condensed into trifluoroethanol to form a 0.4776 M solution. Triflic acid (DOTf) was vacuum distilled from P_2O_5. Trifluoroethanol-d_3 was dried over 3Å molecular sieves for at least 5 d and then was vacuum distilled onto $B(C_6F_5)_3$. After 6 h, the trifluoroethanol-d_3 was vacuum distilled to, and stored in a valved reaction vessel. The platinum dimethyl complexes were synthesized following earlier reported procedures.[2] Ethylbenzene, 1,4-diethylbenzene, and 1,3,5-triethylbenzene were vacuum distilled from Na(0). Benzene was vacuum distilled from sodium benzophenone. *p*-Xylene, allylbenzene, cyclohexene were vacuum distilled from CaH. 1-Pentene was vacuum distilled from lithium aluminum hydride. Cyclohexane and *n*-pentane were vacuum distilled from sodium benzophenone. Methane was dried over alumina for 24 hours before use. Trifluoroethanol-d_3, Lewis acids, substrates, and platinum dimethyl complexes were stored in a Vacuum Atmospheres nitrogen atmosphere dry box.

I. Examination of alternative Lewis acids

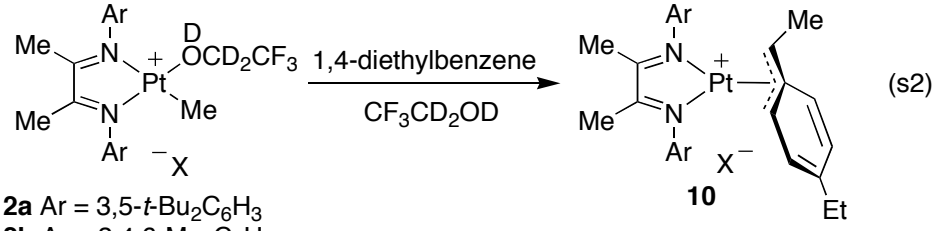


1a Ar = 3,5-*t*-$Bu_2C_6H_3$
1b Ar = 2,4,6-$Me_3C_6H_2$

2

Representative formation of $Ar_2(NN)PtMe^+$ 2a from $Ar_2(NN)PtMe_2$ 1a. To a suspension of platinum dimethyl **1a** (0.010 g, 0.015 mmol) in 0.700 mL of CF_3CD_2OD was added acid (0.015 mmol). The resulting purple mixture was vigorously agitated until a light orange solution was obtained. The solution was transferred to a J. Young tube and analyzed for formation of platinum methyl cation **2a** using ^1H NMR spectroscopy: ^1H NMR (300 MHz, CF_3CD_2OD) δ 7.62 (t, J = 1.8 Hz, 1H), 7.54 (t, J = 1.8 Hz, 1H), 7.04 (d, J = 1.5 Hz, 2H), 6.85 (d, J = 1.5 Hz, 2H), 2.00 (s, 3H), 1.87 (s, 3H), 1.37 (s, 18H), 1.36 (s, 18H), 0.74 (Pt–CH_3, s, 3H, $J_{Pt–H}$ = 63.0 Hz), 0.73 (Pt–CDH_2, s). The ^1H NMR data matched that reported by Zhong, Labinger, and Bercaw.[3]

$Ar_2(NN)PtMe^+$ 2b. To a suspension of platinum dimethyl **1b** (0.0080 g, 0.015 mmol) in 0.700 mL of CF_3CD_2OD was added acid (0.015 mmol). The resulting purple mixture was vigorously agitated until a light orange solution was obtained. The solution was transferred to a J. Young tube and analyzed for formation of platinum methyl cation **2b** using ^1H NMR spectroscopy: ^1H NMR (300 MHz, CF_3CD_2OD) δ 7.12 (s, 2H), 7.06 (s, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.84 (s, 6H), 2.15 (s, 6H), 1.90 (s, 3H), 1.74 (s, 3H), 0.65 (Pt–CH_3, s, 3H, $J_{Pt–H}$ = 69.0 Hz), 0.63 (Pt–CDH_2, s). The ^1H NMR data matched that reported by Zhong, Labinger, and Bercaw.[3]



2a Ar = 3,5-*t*-$Bu_2C_6H_3$
2b Ar = 2,4,6-$Me_3C_6H_2$

10

Representative formation of η^3-benzyl complex 10a from $Ar_2(NN)PtMe^+$ 2a. To a light orange solution of platinum methyl cation **2a** (0.015 mmol) in 0.700 mL of trifluoroethanol-d_3 was added 0.025 mL of 1,4-diethylbenzene (0.16 mmol). The progress of the reaction was monitored periodically using ^1H NMR spectroscopy. After 15 h, ^1H NMR spectroscopy analysis revealed complete consumption of **2a** and formation of η^3-product **10a** (in situ characterization data): ^1H NMR (300 MHz, CF_3CD_2OD) δ 7.61 (s, 1H), 7.59 (s, 1H), 7.24 (br s, 1H), 7.45 (s, 1H), 6.96 (br s, 2H), 6.80 (br s, 1H), 6.47 (s, 1H), 6.39 (s, 1H), 5.88 (d, J = 6.6 Hz, 1H), 2.82 (q, J = 6.6 Hz, 1H), 2.08 (dd, J = 14.7, 7.5 Hz, 1H), 2.02 (s, 3H), 2.00 (dd, J = 14.7, 7.5 Hz, 1H), 1.93 (s, 3H), 1.44 (s, 9H), 1.39 (br s, 9H), 1.36 (br s, 9H), 1.30 (s, 9H), 0.93 (t, J = 7.5 Hz, 3H), 0.29 (d, J = 6.6 Hz, 3H). The ^1H NMR data matched that reported by Driver, Heyduk, Labinger, and Bercaw.[4,5]

η^3-Benzyl complex 10b. To a light orange solution of platinum methyl cation **2a** (0.015 mmol) in 0.700 mL of trifluoroethanol-d_3 was added 0.025 mL of 1,4-diethylbenzene (0.16 mmol). The progress of the reaction was monitored periodically using ^1H NMR spectroscopy. After 15 h, the reaction mixture was cooled and ^1H NMR spectroscopy analysis revealed complete consumption of **2a** and formation of η^3-product **10a** (in situ characterization data): ^1H NMR (300 MHz, CF_3CD_2OD) δ 7.13 (s, 1H), 7.12 (s, 1H), 7.06 (s, 1H), 6.96 (AB

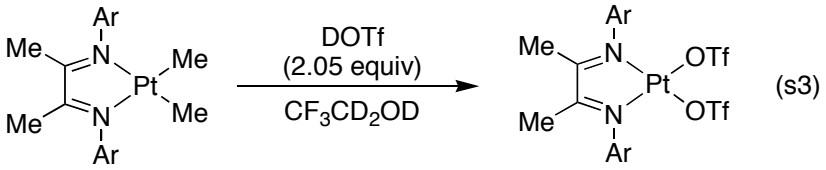
splitting, 1H), 6.91 (s, 1H), 6.05 (s, 1H), 6.05 (d, J = 5.8 Hz, 1H), 5.62 (d, J = 6.0 Hz, J_{PtH} = 23 Hz, 1H), 2.76 (q, J = 6.6 Hz, J_{PtH} = 33 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 6H), 2.18 (s, 3H), 2.16 (m, 1H), 2.07 (m, 1H), 1.96 (s, 3H), 1.89 (s, 3H), 1.85 (s, 3H), 1.46 (s, 3H), 1.03 (t, J = 7.2 Hz, 3H), 0.32 (d, J = 6.6 Hz, 3H). The ^{1}H NMR data matched that reported by Driver, Heyduk, Labinger, and Bercaw.[4,5]

Table s1. Effect of counterion on yield of η^3-benzyl complex complex formation

Entry	Ar	Counterion (X^-)	% Yield[a]
1	3,5-*t*-$Bu_2C_6H_3$ **2a**	$(F_5C_6)_3BOCD_2CF_3$	>95
2	3,5-*t*-$Bu_2C_6H_3$ **2a**	OTf	74
3	3,5-*t*-$Bu_2C_6H_3$ **2a**	$N(Tf)_2$	>95
4	3,5-*t*-$Bu_2C_6H_3$ **2a**	$F_3BOCD_2CF_3$	72
5	3,5-*t*-$Bu_2C_6H_3$ **2a**	OAc	0
6	3,5-*t*-$Bu_2C_6H_3$ **2a**	O_2CCF_3	0
7	2,4,6-$Me_3C_6H_2$ **2b**	$(F_5C_6)_3BOCD_2CF_3$	>95
8	2,4,6-$Me_3C_6H_2$ **2b**	OTf	90
9	2,4,6-$Me_3C_6H_2$ **2b**	$N(Tf)_2$	77
10	2,4,6-$Me_3C_6H_2$ **2b**	$F_3BOCD_2CF_3$	65
11	2,4,6-$Me_3C_6H_2$ **2b**	OAc	0
12	2,4,6-$Me_3C_6H_2$ **2b**	O_2CCF_3	0

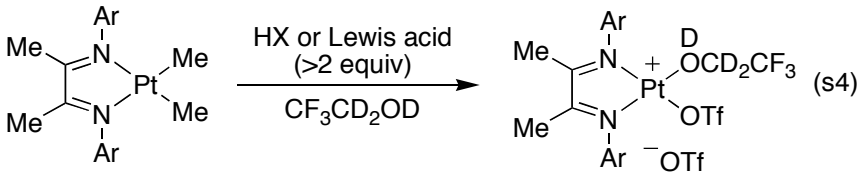
[a] Yields were determined from comparison to the peak area of $CF_3C\mathbf{H}DOD$.

*II. Diprotonolysis of platinum dimethyl **1** with triflic acid or BF_3*



1a Ar = 3,5-*t*-$Bu_2C_6H_3$ **6a** Ar = 3,5-*t*-$Bu_2C_6H_2$

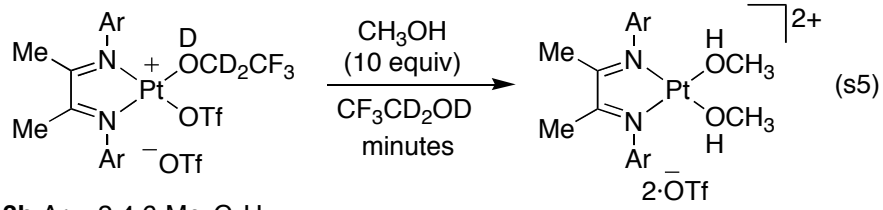
Formation of platinum triflate 3a from platinum dimethyl 1a. To a suspension of platinum dimethyl **1a** (0.010 g, 0.015 mmol) in 0.550 mL of trifluoroethanol-d_3 was added 0.150 mL of a 0.200 M solution of triflic acid-d_1 (DOTf) in trifluoroethanol-d_3. The purple suspension was vigorously agitated until a light orange homogeneous solution was obtained. A portion (0.700 mL) of the solution was transferred to a J. Young tube and the reaction progress was analyzed periodically using ^{1}H NMR spectroscopy. After 20 minutes, ^{1}H NMR spectroscopy analysis revealed complete consumption of **1a** and formation of **6a** (in situ characterization data): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.68-7.89 (br s, 2H), 7.07-7.26 (br s, 4H), 2.07-2.34 (br s, 6H), 1.37 (s, 36H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 187.8, 157.3, 155.9, 144.1, 117.7, 36.7, 31.6, 20.4; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –75.0 (br s), –77.0 (br s).



1b Ar = 2,4,6-$Me_3C_6H_2$ **3b**

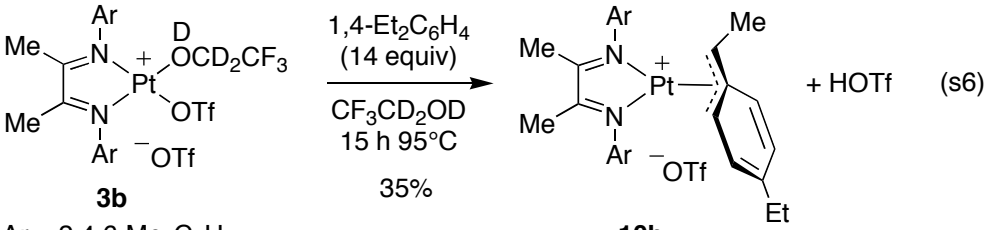
Formation of platinum triflate 3b from platinum dimethyl 1b. To a suspension of platinum dimethyl **1b** (0.0210 g, 0.122 mmol) in 1.00 mL of trifluoroethanol-d_3 was added 0.400 mL of a 0.200 M solution of DOTf in trifluoroethanol-d_3. The red suspension was vigorously agitated until a light orange homogeneous solution

was obtained. A portion (0.700 mL) of the solution was transferred to a J. Young tube and the reaction progress was analyzed periodically using ^{1}H NMR spectroscopy. After seven hours, ^{1}H NMR spectroscopy analysis revealed complete consumption of **1b** and formation of **3b** (in situ characterization data): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.17 (s, 2H), 7.07 (s, 2H), 2.34 (s, 6H), 2.33 (s, 3H), 2.29 (s, 9H), 2.17 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 188.1, 187.6, 144.3, 143.8, 140.0, 139.6, 132.4, 131.9, 131.7, 131.6, 21.32, 21.30, 19.77, 19.72, 18.25, 18.15; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –75.2, –78.6.



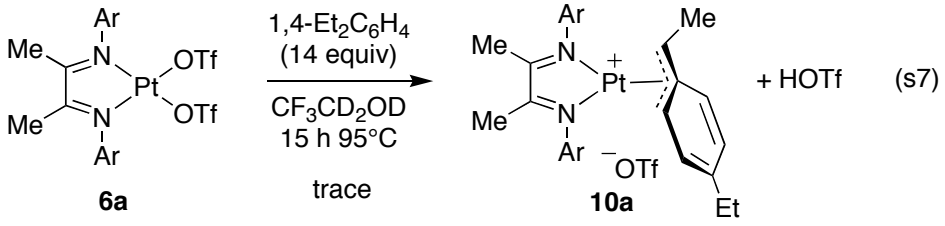
3b Ar = 2,4,6-$Me_3C_6H_2$ **4b**

Methanolysis of platinum triflate 4b. To a light orange solution of platinum triflate **4b** (0.122 mmol) was added 0.0250 mL of methanol (0.617 mmol). After five minutes, ^{1}H NMR spectroscopy analysis revealed complete consumption of unsymmetrical **3b** and formation of symmetrical **4b** (in situ characterization data): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.18 (s, 4H), 2.35 (s, 18H), 2.22 (s, 6H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 188.3, 144.4, 139.9, 132.4, 131.6, 58.5, 21.4, 19.8, 18.2; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –78.6.



3b Ar = 2,4,6-$Me_3C_6H_2$ **10b**

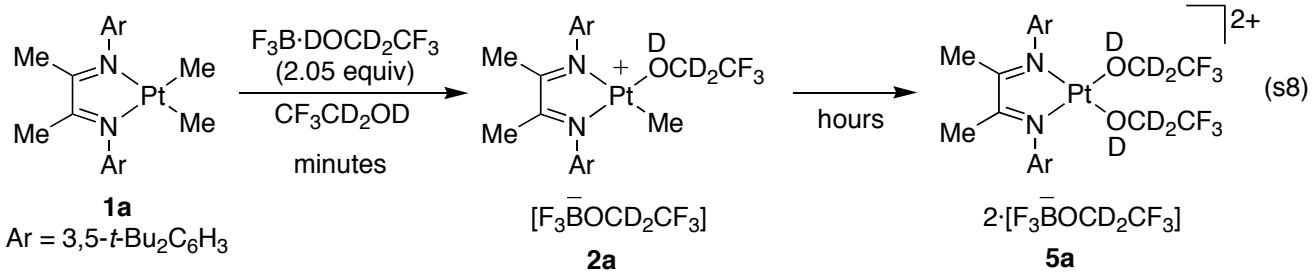
Formation of η^3-benzyl complex 10b from platinum triflate 3b. To 0.700 mL of a 0.0275 M solution of platinum triflate **3b** in a J. Young tube was added 0.040 mL of 1,4-diethylbenzene (0.257 mmol). [The solution of **3b** was prepared by suspending 0.021 g of platinum dimethyl complex **1b** (0.038 mmol) in 1.400 mL of trifluoroethanol-d_3 and adding 0.400 mL of a 0.200 M solution of DOTf in trifluoroethanol-d_3] The resulting mixture was heated to 95 °C. The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 15 h, the reaction mixture was cooled and ^{1}H NMR spectroscopy analysis revealed partial consumption of **3b** and formation of η^3-product **10b** in 35% yield. Prolonged heating or the addition of basic additives did not improve the conversion.



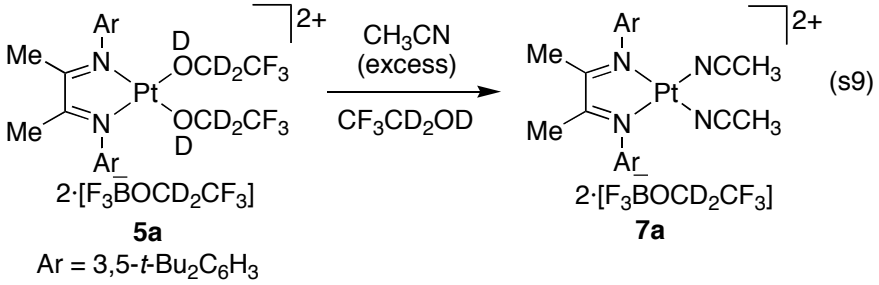
6a Ar = 3,5-*t*-$Bu_2C_6H_2$ **10a**

Reactivity of platinum triflate 6a towards 1,4-diethylbenzene. To a light yellow solution of platinum triflate **3a** in a J. Young tube was added 0.015 mL of 1,4-diethylbenzene (0.096 mmol). [The solution of **3a** was prepared by suspending 0.010 g of platinum dimethyl complex **1a** (0.015 mmol) in 0.550 mL of

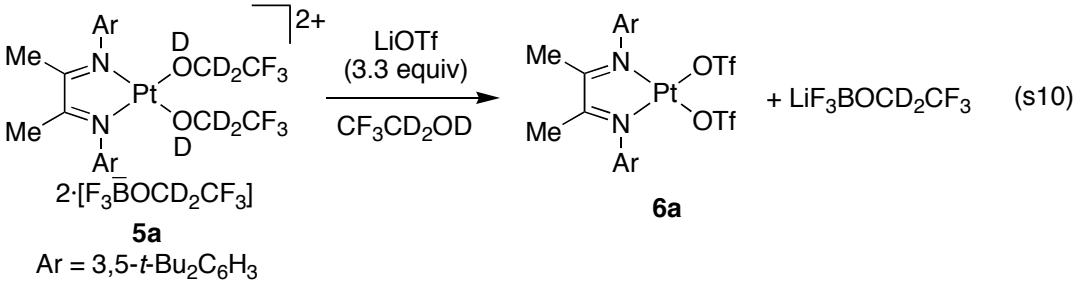
trifluoroethanol-d_3 and adding 0.400 mL of a 0.200 M solution of DOTf in trifluoroethanol-d_3] The resulting mixture was heated to 95 °C. After 15h, the reaction mixture was cooled and ^{1}H NMR spectroscopy analysis revealed partial formation of **10a** (7%). Prolonged heating did not improve the conversion.



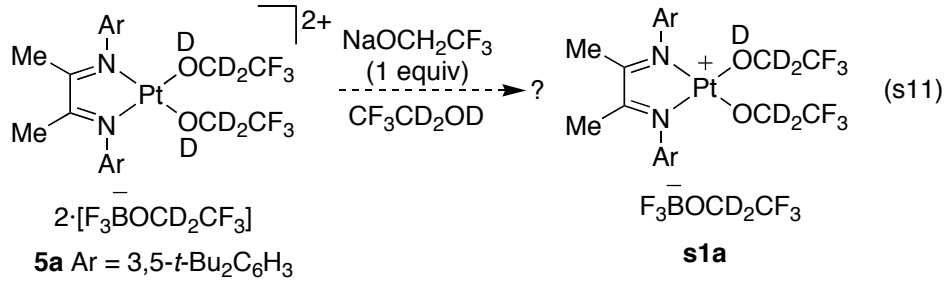
Double protonation of platinum dimethyl 1a with $F_3B{\cdot}DOCD_2CF_3$. To a suspension of platinum dimethyl **1a** (0.010 g, 0.015 mmol) in 0.700 mL of trifluoroethanol-d_3 was added 0.070 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. The reaction progress was analyzed periodically using ^{1}H NMR spectroscopy. After 15 h, analysis revealed complete consumption of **1a** and formation of **5a** (in situ characterization): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.84 (br s, 2H), 7.35 (br s, 4H), 2.32 (br s, 6H), 1.38 (br s, 36H); ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 189.8, 157.9, 144.6, 127.8, 117.9, 37.0, 31.8, 20.6; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –77.3, –150.5 (br s).



Addition of acetonitrile to platinum dication 5a. To a light orange solution of platinum dication **5a** (0.0225 mmol) was added 0.050 mL of acetonitrile (0.957 mmol). The resulting orange solution was concentrated *in vacuo* to 0.023 g of a yellow crystalline solid (93%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.52 (t, J = 1.8 Hz, 2H), 7.25 (d, J = 1.5 Hz, 4H), 2.33 (s, 6H), 2.10 (s, 6H), 1.35 (s, 36H), ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 188.9, 156.9, 145.4, 124.7, 122.5, 117.4, 37.0, 32.0, 21.0, 2.5; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –77.3, –151.3 (br s).



Addition of triflate to platinum dication 5a. To 0.700 mL of a 0.014 M solution of platinum dication **5a** was added 0.0050 g of LiOTf (0.032 mmol). ^{1}H NMR spectroscopy analysis revealed complete consumption of **5a** and formation of symmetrical **6a**. To the resulting reaction mixture was added 0.040 mL of 1,4-diethylbenzene (0.257 mmol). The mixture was heated to 50 °C. After 24 h, the reaction mixture was cooled to room temperature, and ^{1}H NMR spectroscopy analysis revealed partial conversion to η^3-benzyl **10a** (26%).

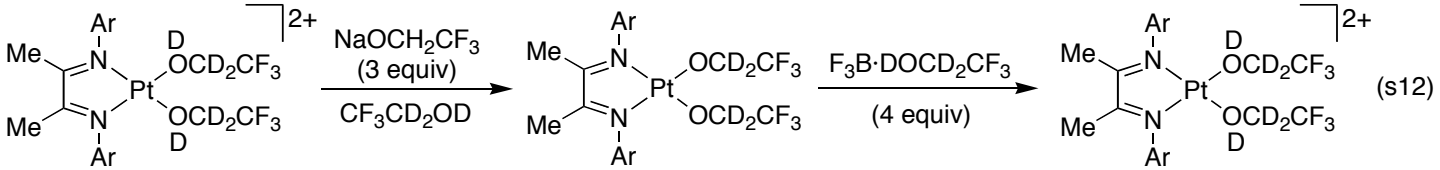


2·[$F_3BOCD_2CF_3$]

5a Ar = 3,5-*t*-$Bu_2C_6H_3$

s1a

Effect of pH on the structure of platinum dication 5a. To 0.0019 g of $NaOCH_2CF_3$ (0.015 mmol) was added 0.700 of a 0.020 M solution of platinum dication **5a** in trifluoroethanol-d_3. The light orange solution immediately turned dark red. ^{1}H NMR spectroscopy analysis revealed consumption of **5a** and formation of **s1a** (in situ characterization). ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.76 (br s, 2H), 7.14 (br s, 4H), 1.82 (s, 6H), 1.37 (br s, 36H).



2·[$F_3BOCD_2CF_3$]

5a Ar = 3,5-*t*-$Bu_2C_6H_3$

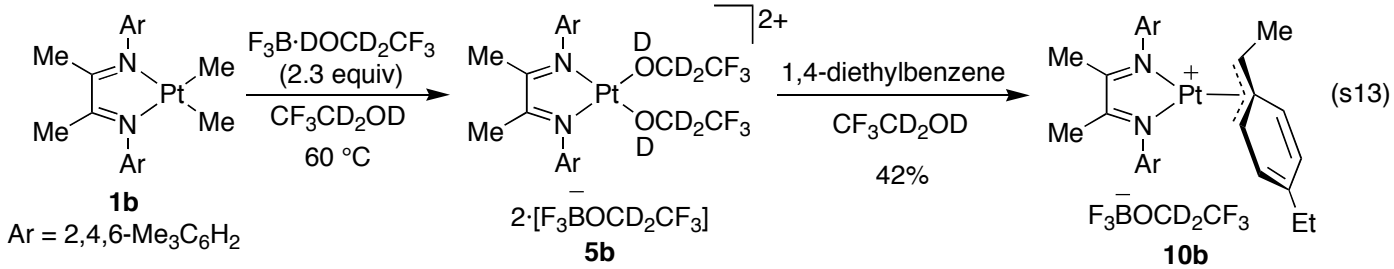
s2a

2·[$F_3BOCD_2CF_3$]

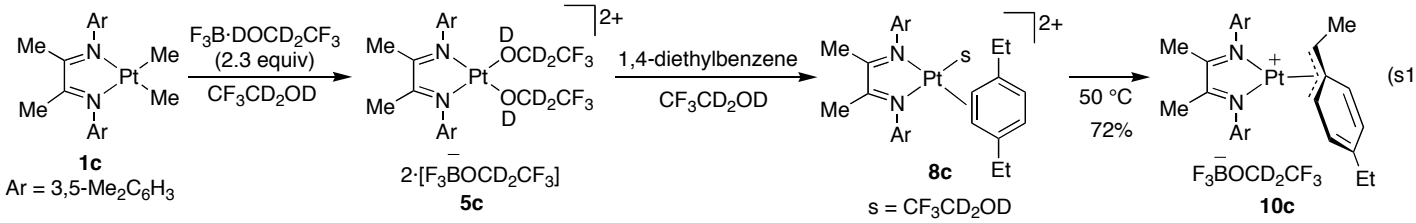
5a

Effect of pH on the structure of platinum dication 5a–dual deprotonation. To 0.0051 g of $NaOCH_2CF_3$ (0.043 mmol) was added 0.700 mL of a 0.015 M solution of platinum dication **5a** in trifluoroethanol-d_3. The light orange solution immediately turned dark red and a white precipitate formed. ^{1}H NMR spectroscopy analysis revealed complete consumption of **5a** and formation of **s2a** (in situ characterization): ^{1}H NMR (500 MHz, CF_3CD_2OD) δ 7.66 (t, J = 1.5 Hz, 2H), 7.06 (d, J = 1.8 Hz, 4H), 1.72 (s, 6H), 1.37 (s, 36H); ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 181.5, 155.2, 146.7, 125.5, 118.13, 36.6, 31.9, 31.8. Addition of 0.100 mL of a 0.478 M solution of BF_3 in trifluoroethanol-d_3 initiated a color change from dark red to light orange. ^{1}H NMR spectroscopy analysis revealed complete consumption of **s2a** and formation of **5a**.

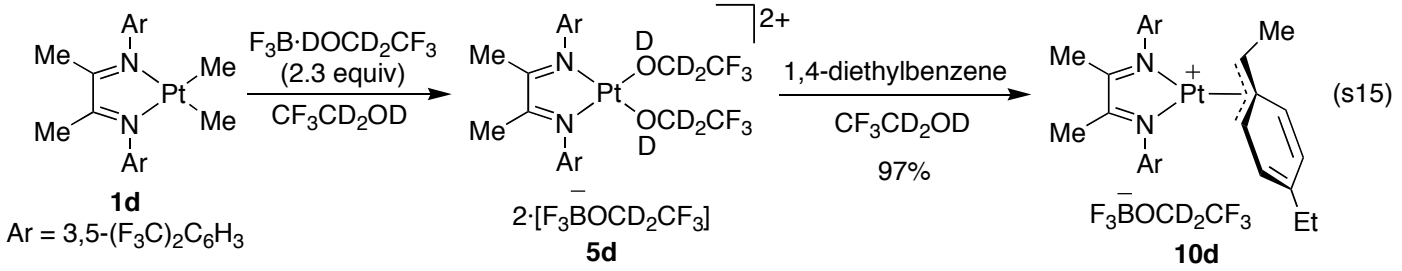
III. Generality of double protonation of $Ar_2(NN)PtMe_2$ with $F_3B{\cdot}DOCD_2CF_3$ and reactivity of platinum dications



Reactivity of platinum dication 5b. To a purple suspension of platinum dimethyl **1b** (0.0080 g, 0.015 mmol) was added 0.070 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation, the suspension became a light orange homogeneous solution. The reaction mixture was heated to 40 °C. After 16 h, the reaction mixture was cooled to room temperature, and ^{1}H NMR analysis revealed only partial consumption of platinum methyl cation **2b** (50%). The reaction mixture was heated to 60 °C. After 9 h, ^{1}H NMR analysis revealed complete consumption of **2b** and the formation of several new platinum complexes (in situ characterization): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 6.95-7.20 (m, 4H), 2.37 (s, 3H), 2.34 (s, 9H), 1.97 (s, 3H), 1.89 (s, 3H). To the reaction mixture was added 0.040 mL of 1,4-diethylbenzene (0.257 mmol) and the resulting mixture was analyzed ^{1}H NMR spectroscopy: no new platinum complexes were observed. The reaction mixture was heated to 50 °C. After 35 h, ^{1}H NMR analysis revealed partial formation of η^3-benzyl complex (42%). Prolonged heating did not improve the conversion.

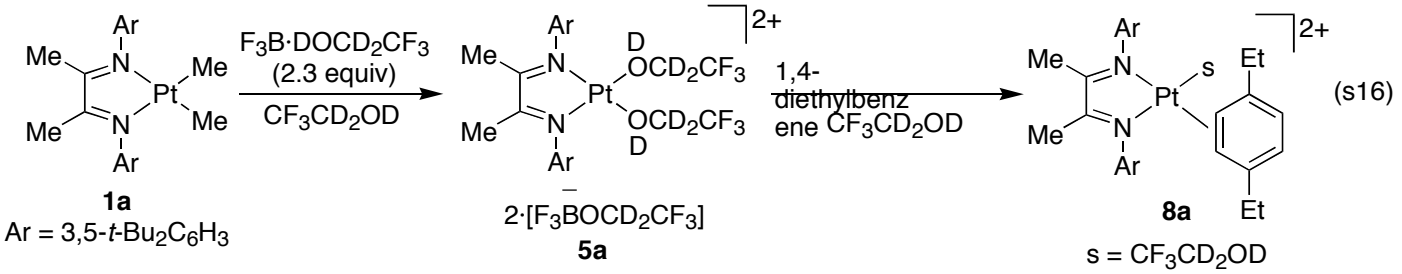


Reactivity of platinum dication 5c. To a purple suspension of platinum dimethyl **1c** (0.0077 g, 0.015 mmol) was added 0.080 mL of a 0.455 M solution of F_3B in trifluoroethanol-d_3. After brief agitation, the suspension became a light orange homogeneous solution. After 15 h, ^{1}H NMR analysis revealed complete consumption of platinum methyl cation **2c** and formation of dication **5c** (in situ characterization): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.33 (br s, 2H), 7.08 (br s, 4H), 2.42 (br s, 12H), 2.27 (br s, 6H). To the reaction mixture was added 0.050 mL of 1,4-diethylbenzene (0.321 mmol) and the resulting mixture was analyzed ^{1}H NMR spectroscopy: a mixture of the dication and a π-arene complex was visible. Selected ^{1}H NMR data for the π-arene complex: ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.30 (br s, 2H), 6.91 (br s, 4H), 6.67 (s, 4H), 2.22 (br s, 6H), 2.04 (q, J = 7.5 Hz, 4H), 1.92 (s, 6H). The reaction mixture was heated to 50 °C. After 13 h, ^{1}H NMR analysis revealed formation of η^3-benzyl complex in 72%. Prolonged heating did not improve the conversion. ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.06 (s, 1H), 7.05 (s, 1H), 6.92 (s, 1H), 6.88 (m, 1H), 6.68 (s, 1H), 6.59 (br s, 2H), 6.27 (d, J = 7.2 Hz, 1H), 5.94 (br s, 1H), 5.75 (d, J = 5.7 Hz, J_{PtH} = 48 Hz, 1H), 2.81 (q, J = 6.6 Hz, J_{PtH} = 30 Hz, 1H), 2.39 (br s, 6H), 2.10 (m, 2H), 1.89 (s, 3H), 1.82 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H), 0.38 (d, J = 5.1 Hz, 3H). The ^{1}H NMR data matched that reported by Driver, Heyduk, Labinger, and Bercaw.[4]

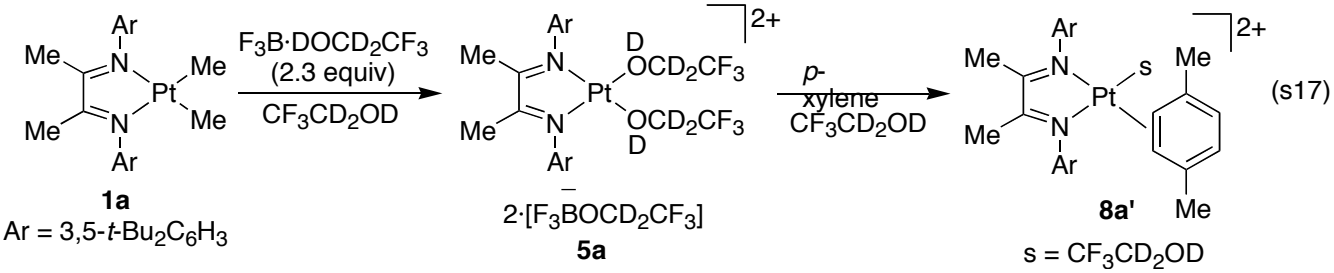


Reactivity of platinum dication 5d. To a suspension of platinum dimethyl **1d** (0.010 g, 0.014 mmol) in 0.630 mL of trifluoroethanol-d_3 was added 0.080 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation, the purple heterogeneous mixture became an orange homogeneous solution. The reaction progress was analyzed periodically using ^{1}H NMR spectroscopy. No consumption of the platinum methyl cation **2d** was observed at prolonged reaction times at 22 °C. The reaction mixture was heated 50 °C. After 36 h, the reaction mixture was cooled to room temperature. ^{1}H NMR spectroscopic analysis revealed a mixture of new platinum complexes: ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 8.08-8.25 (m), 7.94-8.04 (s), 7.90 (d, J = 1.4 Hz), 7.72 (d, J = 1.7 Hz), 2.19-2.34 (br s), 2.08 (s), 2.06 (s), 2.00 (s), 1.97 (s). To the reaction mixture was added 0.050 mL of 1,4-diethylbenzene (0.321 mmol). The resulting mixture was analyzed ^{1}H NMR spectroscopy: no new platinum complexes were observed. The reaction mixture was heated to 60 °C. After 28 h, ^{1}H NMR analysis revealed complete consumption of the mixture of platinum complexes and formation of η^3-benzyl complex (97%). ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 8.06 (s, 1H), 8.04 (s, 1H), 7.94 (br s, 1H), 7.79 (br s, 1H), 7.62 (br s, 2H), 7.07 (s, 2H), 6.40 (s, 1H), 5.95 (d, J = 5.4 Hz, J_{Pt-H} = 48 Hz, 1H), 2.84 (q, J = 5.7 Hz, J_{Pt-H} = 66 Hz, 1H), 2.08 (m, 2H), 2.05 (s, 3H), 1.98 (s, 3H), 0.98 (t, J = 7.5 Hz, 3H), 0.35 (br m, 3H). ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 182.0, 180.2, 150.4, 148.6, 147.7, 143.7, 137.6, 137.5, 136.1, 136.0, 135.8, 135.7, 135.0, 134.9, 129.2, 129.0, 127.7, 126.5, 125.5, 124.1 (br m), 123.4 (2 **C**F_3 br m), 122.3 (br m), 112.8, 72.1, 43.5, 29.7, 20.8, 20.5, 14.5; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –63.3 (3F), –63.4 (3F), –63.6 (6F), –77.2, –81.6, –151.7; HRMS (FAB+) *m / z* calcd for $C_{30}H_{21}D_4N_2F_{12}Pt^+$ [M – {$CF_3CD_2OBF_3$}]$^+$ 840.1725, found 840.1780.

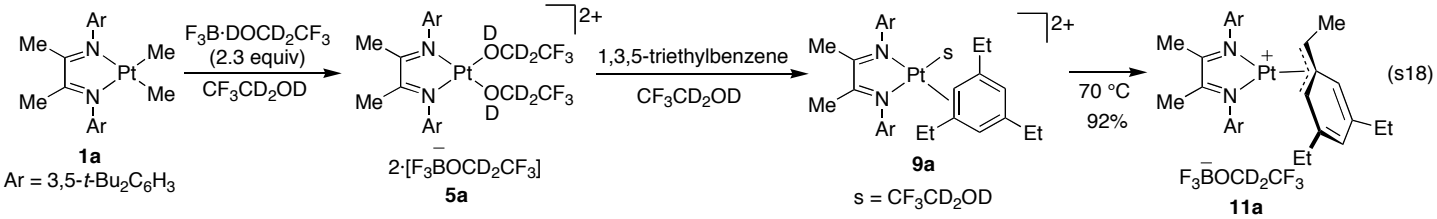
*IV. Reactivity of platinum dication **5a**: observation of π-arene complexes and C–H bond activation.*



π-Arene 8a (R = Et). To a suspension of platinum dimethyl **1a** (0.0149 g, 0.022 mmol) in 0.600 mL of trifluoroethanol-d_3 was added 0.110 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation, the purple heterogeneous mixture became a light orange homogeneous solution. After 9 h, 0.050 mL of 1,4-diethylbenzene (0.321 mmol) to the resulting reaction mixture was added. Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed formation of π-arene complex **8a** (R = Et): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.73 (t, J = 1.8 Hz, 2H), 7.22 (d, J = 1.5 Hz, 4H), 6.77 (s, 4H), 2.41 (s, 6H), 1.88 (q, J = 7.5 Hz, 4H), 1.43 (s, 36H), 1.12 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 181.3, 157.1, 150.4, 143.5, 132.4, 117.0, 113.6; 36.7, 31.9, 27.2, 20.0, 13.0; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –77.2, –150.9. Equilibrium constants were determined by comparison of the diimine methyl signals of both the platinum dication **5a** and π-arene complex **8a** (R = Et).

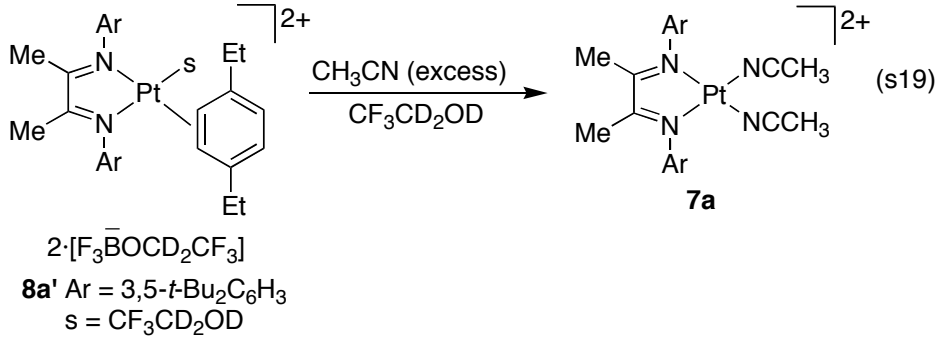


π-Arene 8a' (R = Me). To 0.700 mL of a 0.014 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.011 mL of *p*-xylene (0.0875 mmol). [The solution of **5a** was prepared by dissolving 0.060 g of platinum dimethyl **1a** (0.088 mmol) in 1.60 mL of trifluoroethanol-d_3 and adding 0.400 mL of a 0.478 M solution of BF_3 in trifluoroethanol-d_3.] After brief agitation, the light yellow solution darkened to a light orange. Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed formation of π-arene complex **8a'** (R = Me): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.73 (t, J = 1.3 Hz, 2H), 7.20 (d, J = 1.4 Hz, 4H), 6.87 (s, 4H), 2.43 (s, 6H), 1.51 (s, 6H), 1.41 (s, 36H); ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 181.1, 157.1, 150.1, 136.6, 130.0, 117.2, 115.9, 37.0, 31.9, 19.8, 19.1; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –77.2, –150.7. Equilibrium constants were determined by comparison of the diimine methyl signals of both the platinum dication **5a** and π-arene complex **8a'** (R = Me). The reaction mixture was heated to 50 °C. Periodic analysis of the reaction progress using ^{1}H NMR spectroscopy revealed no formation of η^3-benzyl complex **10a**. Heating the reaction mixture to temperatures in excess of 50 °C did not result in formation of η^3-benzyl complex **10a**. The decomposition of **8a'** (R = Me) into several platinum complexes was observed.

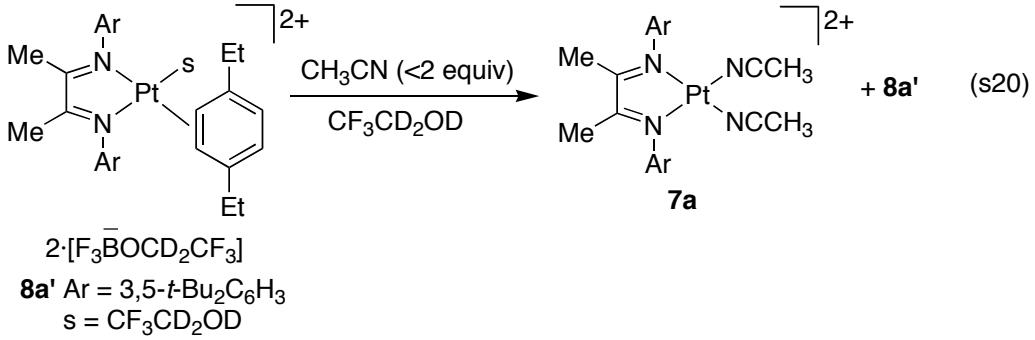


π-Arene 9a. To 0.700 mL of a 0.014 M solution of platinum dication **5a** (0.0097 mmol) in trifluoroethanol-d_3 was added 0.020 mL of 1,3,5-triethylbenzene. [The solution of **5a** was prepared by suspending 0.021 g of platinum dimethyl **1a** (0.030 mmol) in 2.00 mL of trifluoroethanol-d_3.] To the resulting purple suspension was added 0.175 mL of a 0.478 M solution of BF_3 in trifluoroethanol-d_3. The heterogeneous mixture was agitated until a light orange homogeneous solution resulted. After 9 h, the orange solution had faded to a light yellow solution.] Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed partial conversion to π-arene complex **9a** (25%). The reaction mixture was warmed to 50 °C. After 15 h, the orange mixture was cooled to room temperature, and analysis using ^{1}H NMR spectroscopy revealed complete formation of π-arene complex **9a**: ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.74 (t, J = 1.5 Hz, 2H), 7.17 (d, J = 1.8 Hz, 4H), 6.91 (s, 3H), 2.43 (s, 6H), 1.97 (q, J = 7.5 Hz, 6H), 1.43 (s, 36H), 1.71 (t, J = 7.5 Hz, 9H); ^{13}C NMR (125 MHz, CF_3CD_2OD) δ 181.8, 157.2, 149.5, 142.3, 126.7, 121.0, 117.8, 37.2, 32.1, 28.5, 20.4, 13.4; ^{19}F NMR (282 MHz, CF_3CD_2OD) δ –77.3, –151.1. The reaction mixture was heated to 70 °C. After 22 h, the mixture was cooled to room temperature, and analysis ^{1}H NMR spectroscopy revealed partial conversion of π-arene complex **9a** into η^3-benzyl complex **11a** (92%): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.60 (t, J =1.8 Hz, 1H), 7.54 (t, J = 1.5 Hz, 1H), 7.27 (br s, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.81 (br s, 1H), 6.73 (t, J = 1.8 Hz, 1H), 6.67 (br m, 1H, H/D exchange evident), 6.07 (t, J = 1.5 Hz, 1H), (5.58, br m, 1H, H/D exchange evident), 2.74 (q, J = 7.8 Hz, 1H), 1.98 (m, 2H), 1.94 (s, 3H), 1.76 – 1.88 (m, 2H), 1.77 (s, 3H), 1.42 (br s, 9H), 1.39 (s, 9H), 1.38 (br s, 9H), 1.34 (s, 9H), 1.16 (t, J = 7.8

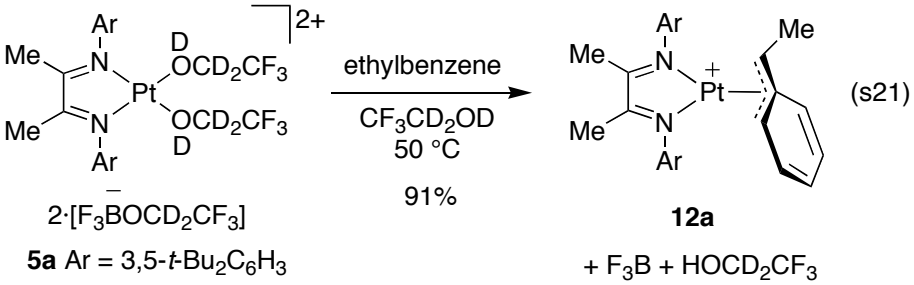
Hz, 3H), 0.87 (t, J = 7.8 Hz, 3H), 0.27 (d, J = 7.8 Hz, 3H); The ^{1}H NMR data matched that reported for **11a** by Driver, Labinger, and Bercaw.[5]



Ligand substitution of π-arene complex with acetonitrile. To a solution of π-arene complex **8a'** (0.012 mmol) was added 0.050 mL of acetonitrile (0.95 mmol). Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed consumption of π-arene complex **8a'** and formation of diacetonitrile adduct **7a**.



Ligand substitution of π-arene complex with acetonitrile. To a solution of π-arene complex **8a'** (0.012 mmol) was added 0.001 mL of acetonitrile (0.019 mmol). Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed partial consumption of π-arene complex **8a'** and formation of diacetonitrile adduct **7a** (63%).



η^3-Benzyl complex 12a. To 0.700 mL of a 0.014 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.025 mL of ethylbenzene (0.200 mmol). [The solution of **5a** was prepared by suspending 0.021 g of platinum dimethyl **1a** (0.030 mmol) in 2.00 mL of trifluoroethanol-d_3 and adding 0.175 mL of a 0.478 M solution of BF_3 in trifluoroethanol-d_3.] The resulting light yellow solution was heated to 50 °C. After 15 h, the reaction mixture was cooled to room temperature, and analysis using ^{1}H NMR spectroscopy revealed complete consumption of **5a** and formation of η^3-benzyl complex **12a** (91%): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.72 (t, J = 1.8 Hz, 1H), 7.37 (t, J = 1.8 Hz, 1H), 7.35 (s, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.03 (s, 1H), 6.89 (br s, 1H), 6.84 (m, 1H), 6.78 (br s, 1H), 6.36 (m, 1H), 6.16 (s, 1H), 5.75 (d, J = 6.6 Hz, J_{Pt-H} = 45 Hz, 1H), 2.86 (q, J = 6.6

Hz, 1H), 2.15 (s, 3H), 2.01 (s, 3H), 1.42 (s, 9H), 1.40 (br s, 9H), 1.36 (br s, 9H), 1.33 (s, 9H), 0.33 (d, J = 6.6 Hz, 3H). The ^{1}H NMR data matched that reported for **12a** by Driver, Labinger, and Bercaw.[5]

V. Mechanism of η^3-benzyl formation: kinetics and isotopic labeling

a. Representative procedure

A stock solution of the platinum dication, **5a**, was generated by diluting a mixture of 0.074 g of platinum dimethyl complex **1a** (0.109 mmol) and 0.550 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3 to 5.00 mL with trifluoroethanol-d_3. Upon dissolution, 0.400 mL of the resulting 0.014 M solution of the platinum dication **5a** was placed in a 1 mL volumetric flask and 0.030 mL of 1,4-diethylbenzene (0.193 mmol) was added. The resulting mixture was diluted to 1.00 mL with trifluoroethanol-d_3 and vigorously agitated. Upon homogeneity, 0.700 mL of the resulting light orange solution was transferred to a J. Young NMR tube, and the mixture was cooled to –10 °C to prevent further reaction. The sample was inserted into the NMR probe, which had come to an equilibrium temperature of 66 °C. After briefly shimming on the sample, an array of spectra was acquired. After completion of the run, the intensity data for relating the concentrations of platinum π-arene **8a'** (R = Et) and η^3-benzyl **10a** were obtained from the NMR spectra and were fit to the first-order exponential equations

$$[1] = Ae^{-k_{obs}t}, \text{ and}$$
$$[2] = A(1 - e^{-k_{obs}t}).$$

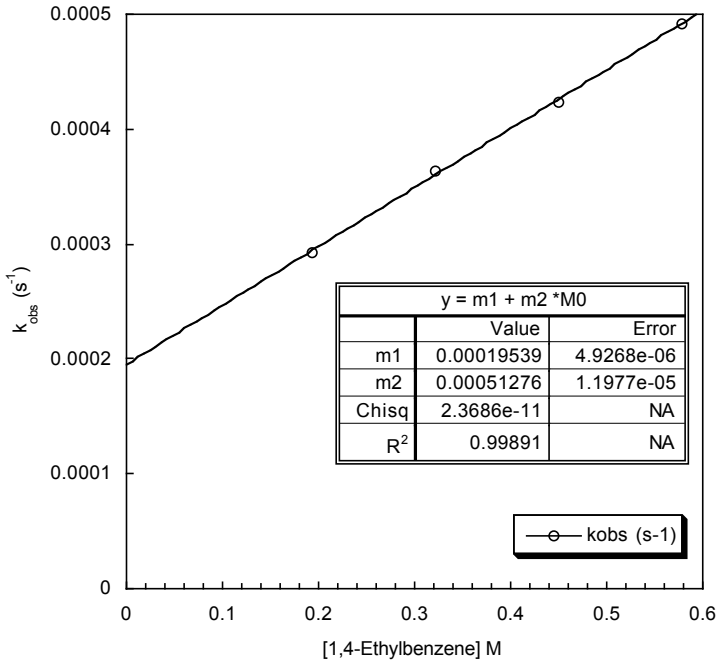
Second-order rate constants were obtained from a plot of k_{obs} vs [1,4-diethylbenzene] over the concentration range 0.193 to 0.578 M. The solubility of 1,4-diethylbenzene limited the concentration range.

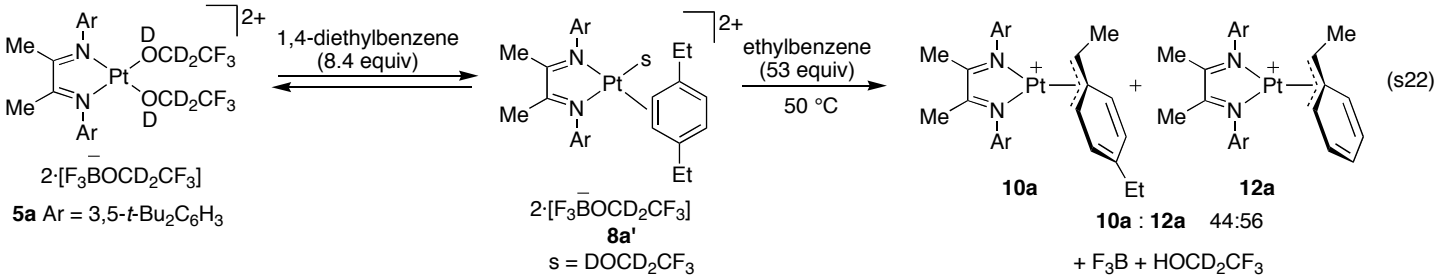
b. Summary of kinetic data

Table s2. 1,4-Diethylbenzene

Entry	L_nPt^{2+}	Substrate	T (°C)	[substrate] (M)	k_{obs} ($\times 10^4$ s^{-1})	R^2-value	Error in equation fit ($\times 10^4$ s^{-1})
1	**8a'** (R=Et)	1,4-$Et_2C_6H_4$	66	0.193	2.92	0.99769	0.06
2	**8a'** (R=Et)	1,4-$Et_2C_6H_4$	66	0.321	3.64	0.99807	0.07
3	**8a'** (R=Et)	1,4-$Et_2C_6H_4$	66	0.450	4.23	0.99549	0.1
4	**8a'** (R=Et)	1,4-$Et_2C_6H_4$	66	0.578	4.91	0.99809	0.1
5	**s4a** (R=Et)	1,4-$Et_2C_6D_4$	66	0.578	3.72	0.99708	0.09
6	**s5a** (R=Et)	1,4-$(CD_3CD_2)_2C_6H_4$	66	0.578	4.28	0.99511	0.1

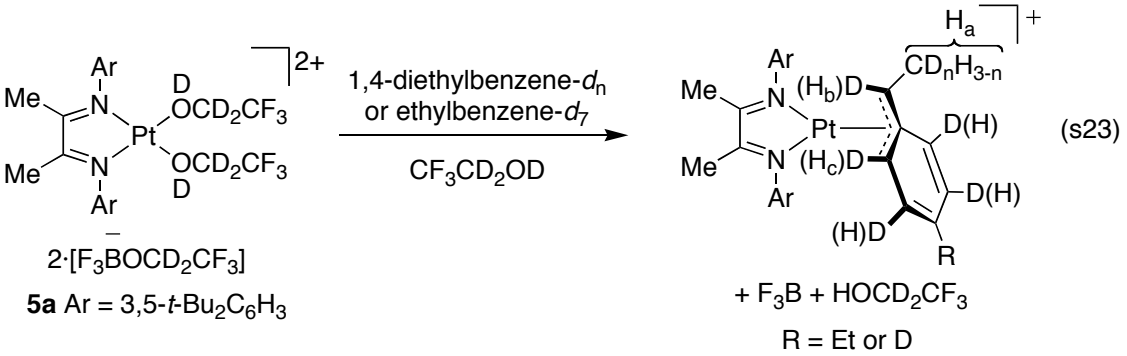
Figure s1. Dependence of [1,4-diethylbenzene] on rate





(s22)

Competition reaction between platinum π-arene 13a (R = Et) and ethylbenzene. To 0.700 mL of a 0.022 M solution of platinum dication **5a** was added 0.020 mL of 1,4-diethylbenzene (0.128 mmol). [The solution of **5a** was prepared by suspending 0.030 g of platinum dimethyl **1a** in 1.5 mL of trifluoroethanol-d_3 and adding 0.185 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. The resulting mixture was diluted to 2 mL.] Analysis of the resulting orange solution using ^{1}H NMR spectroscopy revealed a 46:54 mixture of **5a**:**8a** (R = Et). To this mixture was added 0.100 mL of ethylbenzene. The reaction mixture was heated to 50 °C. After 20 h, the mixture was cooled to room temperature. Analysis using ^{1}H NMR spectroscopy revealed a 44:56 mixture of **10a**:**12a**.



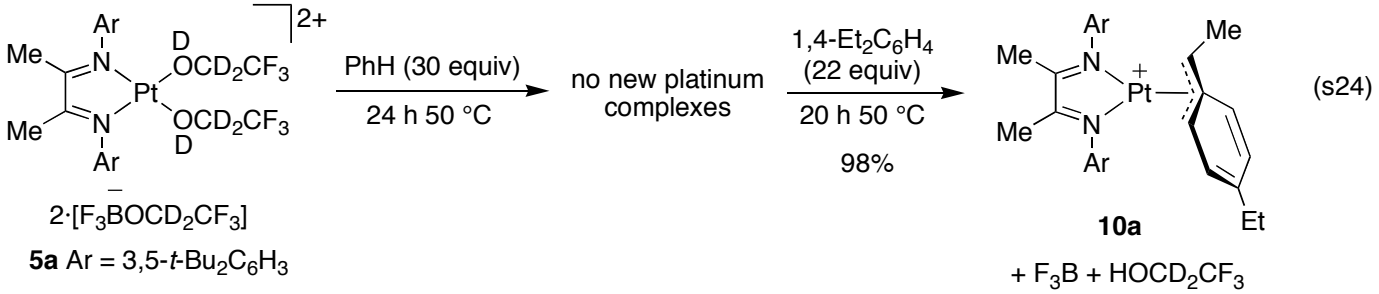
Representative procedure for ethyl- and 1,4-diethylbenzene isotopolog studies. To 0.700 mL of a 0.014 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.016 mL of 1,4-ethylbenzene-d_4 (0.100 mmol). [The solution of **5a** was prepared by suspending 0.021 g of platinum dimethyl **1a** (0.030 mmol) in 2.00 mL of trifluoroethanol-d_3 and adding 0.175 mL of a 0.478 M solution of BF_3 in trifluoroethanol-d_3.] The resulting light yellow solution was heated to 50 °C. After 21 h, the reaction mixture was cooled to room temperature, and analysis using ^{1}H NMR spectroscopy revealed complete consumption of **5a** and formation of η^3-benzyl complex. The peak areas of H_a (0.30 ppm), H_b (2.82 ppm), H_c (5.88 ppm) were compared for H/D isotope exchange. The resulting reaction mixture was filtered through SiO_2 and the resulting clear filtrate was analyzed using GC/MS.

Table s2. Isotope exchange observed employing **5a**

entry	substrate	% Deuterium in η^3-benzyl product			Molecular ion peak observed in GC/MS
		H_a	H_b	H_c	(m/z)
1	1,4-$(CH_3CH_2)_2C_6H_4$	21	*	65	138
2	1,4-$(CD_3CD_2)_2C_6H_4$	96	0	82	148
3	1,4-$(CH_3CH_2)_2C_6D_4$	20	*	87	138
4	$CH_3CH_2C_6H_5$	12	*	20	111
5	$CH_3CD_2C_6D_5$	18	0	94	113

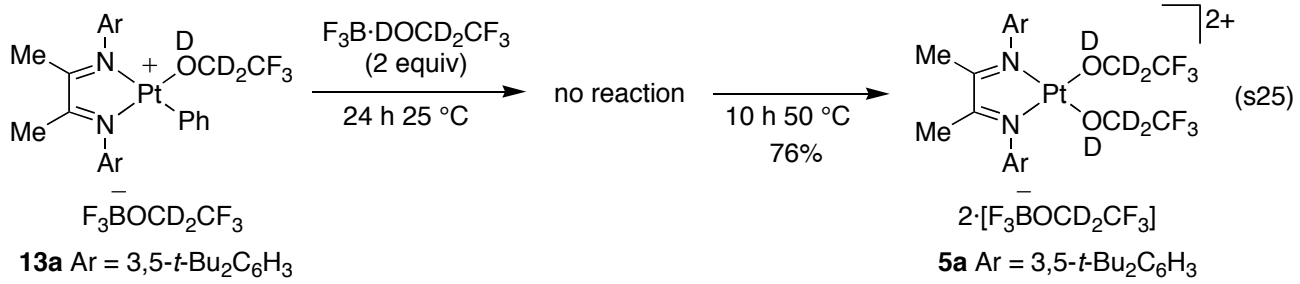
*could not resolve necessary peaks

VI. Other C–H bond activations at dicationic platinum centers



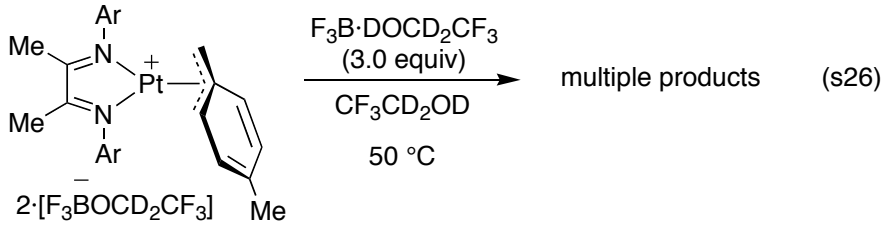
Attempted activation of benzene with platinum dication 5a. To a suspension of platinum dimethyl **1a** (0.012 g, 0.017 mmol) in 0.650 mL of trifluoroethanol-d_3 was added 0.070 mL of a 0.455 M solution of BF_3 in trifluoroethanol-d_3. The resulting purple suspension was agitated until a light orange homogeneous solution resulted. After 16 h, 0.040 mL of benzene (0.440 mmol) was added to the now light yellow solution. The reaction progress (or lack thereof) was analyzed periodically using ^{1}H NMR spectroscopy. The reaction

mixture was heated to 50 °C. After 24 h, the reaction mixture was cooled to room temperature. Analysis using ^{1}H NMR spectroscopy revealed no formation of the platinum phenyl cation. To the reaction mixture was added 0.050 mL of 1,4-diethylbenzene (0.321 mmol). The resulting mixture was heated to 50 °C. After 20 h, the reaction mixture was cooled to room temperature, and the reaction progress was analyzed using ^{1}H NMR spectroscopy: η^3-benzyl complex **10a** was formed in 98% yield.



13a Ar = 3,5-*t*-Bu$_2$C$_6$H$_3$ **5a** Ar = 3,5-*t*-Bu$_2$C$_6$H$_3$

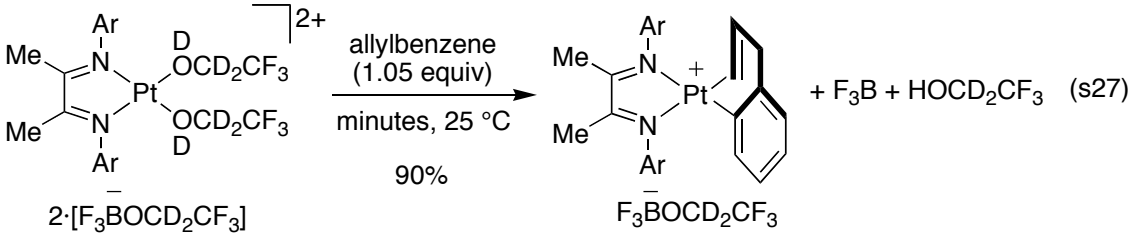
Stability of platinum phenyl cation 13a to reaction conditions. To a suspension of platinum dimethyl **1a** (0.010 g, 0.015 mol) in 0.700 mL of trifluoroethanol-d_3 was added 0.032 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. The purple heterogeneous mixture was agitated. To the resulting orange solution was added 0.010 mL of benzene (0.11 mmol). After 16 h, analysis using ^{1}H NMR spectroscopy revealed consumption of platinum methyl cation **2a** and formation of platinum phenyl cation **13a** (in situ characterization): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.67 (t, J = 1.8 Hz, 1H), 7.22 (t, J = 1.5 Hz, 1H), 7.13 (d, J = 1.7 Hz, 2H), 6.84 (d, J = 6.6 Hz, 2H), 6.63 – 6.70 (m, 3H), 6.60 (d, J = 1.8 Hz, 2H), 2.13 (s, 3H), 1.92 (s, 3H), 1.39 (s, 9H), 1.21 (s, 9H). The ^{1}H NMR data matched that reported for **16a** by Zhong, Labinger, and Bercaw.[3] To the reaction mixture was added 0.040 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After 24 h, analysis using ^{1}H NMR spectroscopy revealed trace formation of platinum dication **5a**. The reaction mixture was heated to 50 °C. After 10 h, analysis using ^{1}H NMR spectroscopy revealed complete consumption of **13a** and formation of platinum dication **5a**.



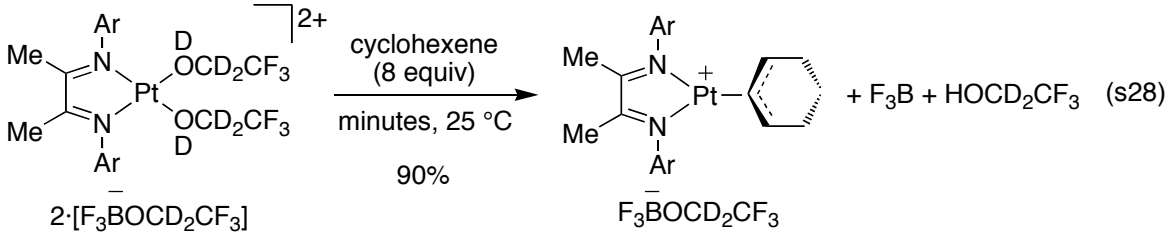
s3a Ar = 3,5-*t*-Bu$_2$C$_6$H$_3$

Stability of platinum η^3-benzyl complex s3a to reaction conditions. To 0.700 mL of a 0.015 M solution of platinum methyl cation **2a** in trifluoroethanol-d_3 was added 0.020 mL of *p*-xylene (0.163 mmol). [The solution of **2a** was prepared by suspending of platinum dimethyl **1a** (0.014 g, 0.020 mmol) in 1.4 mL of trifluoroethanol-d_3. To the purple solution was added 0.050 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. The heterogeneous mixture was agitated until a light orange solution resulted.] The reaction mixture was heated to 50 °C. After 5 h, the mixture was cooled to room temperature. Analysis using ^{1}H NMR spectroscopy revealed complete consumption of platinum methyl cation **2a** and formation of η^3-benzyl complex **s4a** (in situ characterization): ^{1}H NMR (300 MHz, CF_3CD_2OD) δ 7.61 (t, J = 1.5 Hz, 1H), 7.58 (t, J = 1.8 Hz, 1H), 7.06 (br s, 2H, obscured by *p*-xylene signal), 6.69 (d, J = 1.5 Hz, 2H), 6.61 (d, J = 7.2 Hz, 2H), 6.27 (d, J = 7.8 Hz, 2H), 2.62 (s, J_{Pt-H} = 42 Hz, 2H), 2.00 (s, 3H), 1.89 (s, 3H), 1.69 (s, 3H), 1.40 (s, 36 H). The ^{1}H NMR data matched that reported for **16a** by Driver, Labinger, and Bercaw.[5] To this solution was added 0.065 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After 16 h, Analysis using ^{1}H NMR spectroscopy revealed diminishment

of **s3a** by 4%. The reaction mixture was heated to 50 °C. After 20 h, the mixture was cooled to room temperature and analyzed using ^{1}H NMR spectroscopy: 70% of η^3-benzyl complex **s3a** had been consumed to form several new platinum complexes—none of which were platinum dication **5a**.

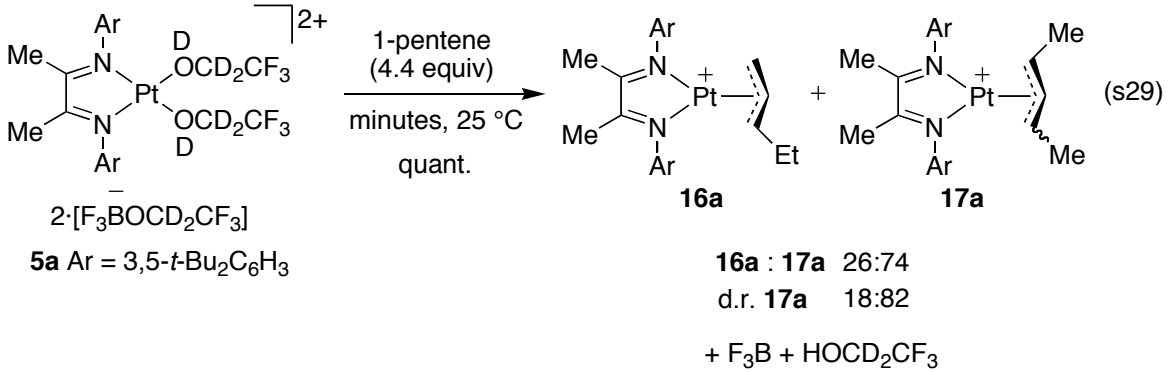


Platinum complex 14a. To a purple suspension of platinum dimethyl **1a** (0.060 g, 0.088 mmol) in 8 mL of trifluoroethanol was added 0.500 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. Upon brief agitation the heterogeneous mixture became an orange homogeneous solution. After 6 h, 0.0125 mL of allylbenzene was added to the resulting light yellow solution. Upon addition, the light yellow solution immediately darkened to a cherry apple red color. After 12 h, the reaction mixture was concentrated *in vacuo* to afford 0.073 g of platinum complex **14a** (90%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.42 (t, J = 1.8 Hz, 1H), 7.32 (t, J = 1.8 Hz, 1H), 7.14 (br s, 1H), 6.89 (t, J = 1.8 Hz, 1H), 6.85 (t, J = 1.8 Hz, 1H), 6.83 (d, J = 7.2 Hz, 1H), 6.65 (td, J = 7.2, 1.2 Hz, 1H), 6.53 (br s, 1H), 6.28 (t, J = 7.2 Hz, 1H), 5.48 (dd, J = 7.8, 1.2 Hz, 1H), 5.10 (dt, J = 13.2, 6.6 Hz, 1H, $J_{Pt–H}$ ~ 75 Hz at 300 MHz), 3.99 (d, J = 14.4 Hz, 1H), 3.91 (dd, J = 17.4, 6.3 Hz, 1H), 3.41 (d, J = 7.8 Hz, 1H, $J_{Pt–H}$ ~ 63 at 300 MHz), 2.72 (d, J = 16.8 Hz, 1H, $J_{Pt–H}$ ~ 114 Hz at 300 MHz), 2.53 (s, 3H), 2.21 (s, 3H), 1.40 (br s, 9H), 1.38 (s, 9H), 1.34 (s, 9H), 0.94 (br s, 9H); ^{13}C NMR (150.8 MHz, CD_2Cl_2) δ 184.1, 179.2, 154.1, 154.0, 148.5, 144.2, 144.1, 137.6, 133.1, 126.4, 124.8, 124.7, 124.2, 122.9, 122.8, 122.5, 119.5, 117.3, 115.6, 114.5, 108.3 ($J_{Pt–C}$ = 205 Hz), 70.0 (J = 205 Hz), 39.2, 35.7, 31.57, 31.53, 31.51, 31.48, 31.1, 21.8, 21.7, 21.03, 21.01; IR (KBr pellet) 3050, 2963, 2871, 1587, 1063, 900, 557 cm^{-1}; UV-Vis (CF_3CH_2OH) 200 nm (ε = 1.62 × 10^5 M^{-1}·cm^{-1}), 219 nm (ε = 9.55 × 10^4 M^{-1}·cm^{-1}), 276 nm (ε = 1.93 × 10^4 M^{-1}·cm^{-1}), 388 nm (ε = 7.76 × 10^3 M^{-1}·cm^{-1}). HRMS (FAB+) m/z calcd for $C_{41}H_{57}N_2Pt^+$ [M – {$CF_3CD_2OBF_3$}]$^+$ 772.4164, found 772.4162.

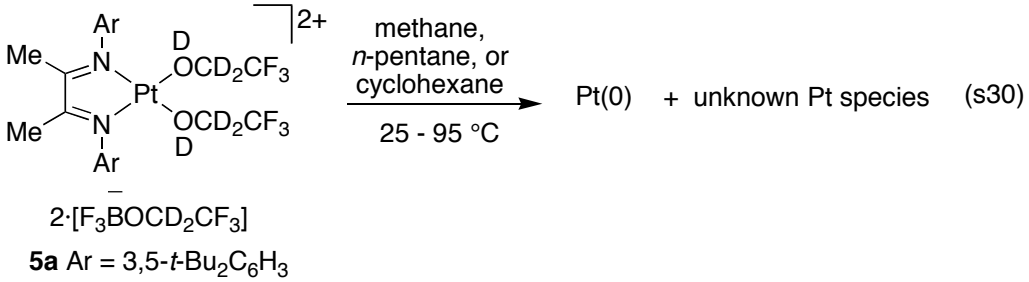


η^3-Allyl 15a. To a purple suspension of platinum dimethyl **1a** (0.060 g, 0.0875 mmol) in 8 mL of trifluoroethanol was added 0.500 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation, the heterogeneous mixture became an orange homogeneous solution. After 6 h, 0.018 mL of cyclohexene (0.175 mmol) was added to the resulting light yellow solution. After 12 h, the light orange solution was concentrated *in vacuo* to afford 0.071 g of η^3-allyl **15a** as a light yellow powder (90%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.41 (t, J = 1.8 Hz, 2H), 6.99 (br s, 4H), 5.33 (t, J = 6.3 Hz, 1H, $J_{Pt–H}$ = 84 Hz), 4.12 (t, J = 6 Hz, 2H, $J_{Pt–H}$ = 33Hz), 2.28 (s, 6H), 1.97 – 2.1 (m, 2H), 1.42 – 1.55 (m, 2H), 1.34 (s, 36H), 0.62 – 0.82 (m, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 177.5, 153.4, 148.7, 122.4, 115.2, 100.7, 63.1 ($J_{Pt–C}$ = 242 Hz), 35.7, 31.6, 30.2, 20.4, 19.4; IR (KBr pellet) 2961, 2870, 1595, 1364, 1064, 928, 711 cm^{-1}; UV-Vis (CF_3CH_2OH) 202 nm (ε =

1.17 × 10^5 $M^{-1}\cdot cm^{-1}$), 219 nm (ε = 7.30 × 10^4 $M^{-1}\cdot cm^{-1}$), 276 nm (ε = 2.32 × 10^4 $M^{-1}\cdot cm^{-1}$). HRMS (FAB+) *m / z* calcd for $C_{38}H_{57}N_2Pt^+$ [M – {$CF_3CD_2OBF_3$}]$^+$ 736.4170, found 736.4195.



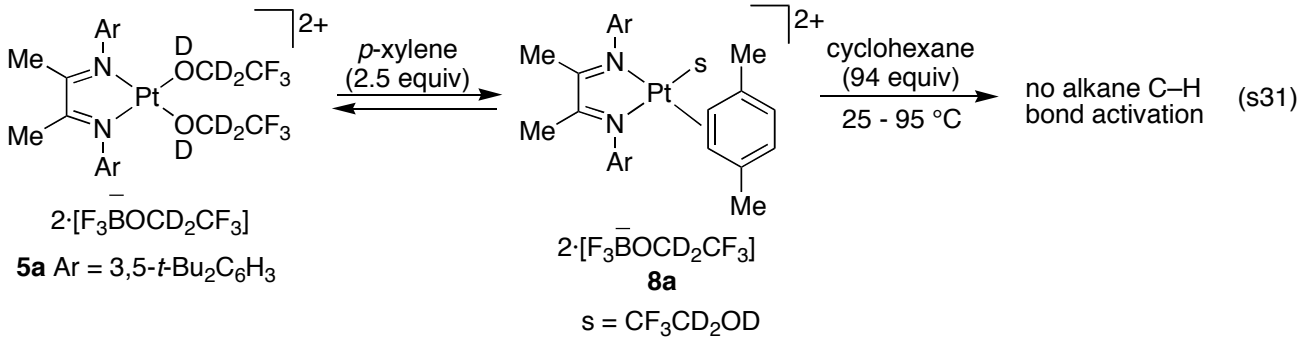
η^3-Allyls 16a and 17a. To 0.700 mL of a 0.015 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.006 mL of 1-pentene. [The solution of **5a** was prepared by suspending 0.022 g of platinum dimethyl **1a** (0.032 mmol) in 2.0 mL of trifluoroethanol-d_3. To the resulting purple heterogeneous mixture was added 0.175 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation the mixture became a light orange solution. After 6 h, the orange solution had faded to light yellow.] After 20 min, analysis of the reaction progress using ^{1}H NMR spectroscopy revealed complete consumption of **5a** and formation of a 26:74 mixture of η^3-allyls **16a** and **17a** (>95%). The diastereoselectivity of **17a** was determined to be 18:82 by comparison of doublets at 0.37 and 0.24 respectively. Major diastereomer of η^3-allyl **17a**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38 (t, *J* = 1.5 Hz, 2H), 7.01 (br s, 2H), 6.76 (br s, 2H), 4.35 (t, *J* = 11.5 Hz, 1H, J_{Pt-H} = 74 Hz), 3.18 (sextet, *J* = 6.5 Hz, 2H, J_{Pt-H} = 88 Hz), 2.23 (s, 6H), 1.35 (s, 18H), 1.31 (s, 18H), 0.25 (d, *J* = 6 Hz, 6H); ^{13}C NMR (125.7 MHz, CD_2Cl_2) δ 177.9, 154.3, 154.0, 147.6, 122.0, 114.9, 111.3, 108.6, 61.6 (J_{Pt-C} = 243 Hz), 35.71, 35.65 31.56, 31.54, 20.3, 15.0. Selected data for regioisomer **16a**: ^{1}H NMR (500 MHz, CF_3CD_2OD) δ 4.65 (dt, *J* = 11.5 Hz, 1H, J_{Pt-H} ~75 Hz), 3.71 (t, *J* = 6.5 Hz, 1H, J_{Pt-H} ~ 28 Hz), 2.79 (dd, *J* = 12.0, 2.5 Hz, 1H, J_{Pt-H} ~ 65 Hz), 0.71 (t, *J* = 7 Hz, 3H). Selected data for the minor diastereomer **17a**: ^{1}H NMR (500 MHz, CF_3CD_2OD) δ 4.28 (*t*, *J* = 7 Hz, 1H), 3.32 (dt, *J* = 19.5 Hz, 7H, 2H, J_{Pt-H} ~ 81 Hz), 0.37 (d, *J* = 6 Hz, 6H). IR (KBr pellet) 2961, 2871, 2587, 1595, 1466, 1061, 522 cm^{-1}; UV-Vis (CF_3CH_2OH) 200 nm (ε = 7.70 × 10^4 $M^{-1}\cdot cm^{-1}$), 219 nm (ε = 4.68 × 10^4 $M^{-1}\cdot cm^{-1}$), 274 nm (ε = 9.77 × 10^3 $M^{-1}\cdot cm^{-1}$), 381 nm (ε = 6.70 × 10^3 $M^{-1}\cdot cm^{-1}$). HRMS (FAB+) *m / z* calcd for $C_{37}H_{57}N_2Pt^+$ [M – {$CF_3CD_2OBF_3$}]$^+$ 724.4170, found 724.4148.



Attempted C–H bond activation of cyclohexane and *n*-pentane. To 0.700 mL of a 0.015 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.011 mL of cyclohexane. [The solution of **5a** was prepared by suspending 0.021 g of platinum dimethyl **1a** (0.031 mmol) in 2.0 mL of trifluoroethanol-d_3. To the resulting purple heterogeneous mixture was added 0.175 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation the mixture became a light orange solution. After 13 h, the orange solution had faded to light yellow.] The reaction progress (or lack thereof) was analyzed periodically using ^{1}H NMR spectroscopy.

The resulting yellow solution was heated to 50 °C. After 20 h, the reaction mixture was cooled to room temperature and was analyzed using ^{1}H NMR spectroscopy: no H/D isotope exchange was visible in the cyclohexane peak at 1.47 ppm and little consumption of **5a** had occurred. The reaction mixture was heated to 95 °C. After 30 h, the reaction mixture was cooled and analyzed using ^{1}H NMR spectroscopy: no H/D exchange in cyclohexane was apparent. 80% of platinum dication **5a** had been consumed. Several new platinum species were visible (Diagnostic methyl singlets at (^{1}H NMR 300 MHz, CF_3CD_2OD δ 1.91, 1.88, and 1.83 ppm). Analysis of the reaction mixture using LRMS (ESI, methanol) revealed a major mass fragment at 685 *m / z* and a minor fragment at 1357 *m / z*. These same platinum species were formed when the platinum dication **5a** was heated to 95 °C for 30 h in the absence of substrate. The same procedure was followed using 0.012 mL of *n*-pentane. Identical results were obtained: no apparent H/D isotope exchange and only decomposition of the platinum complex was obtained.

Attempted C–H bond activation of methane. To a purple suspension of platinum dimethyl **1a** (0.022 g, 0.032 mmol) in 2.0 mL of trifluoroethanol-d_3 was added 0.150 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation, the heterogeneous mixture became a light orange solution. After 19 h, 0.500 mL of the resulting 0.014 M solution of platinum dication **5a** was placed in a specially designed high-pressure single crystal sapphire NMR tube.[6] The resulting mixture was pressured with 475 psi of methane (1.86 mmol). The reaction progress (or lack thereof) was analyzed periodically using ^{1}H NMR spectroscopy. The resulting yellow solution was heated to 50 °C. After 20 h, the reaction mixture was cooled to room temperature and was analyzed using ^{1}H NMR spectroscopy: no H/D isotope exchange was visible in the methane peak at 0.17 ppm and little consumption of **5a** had occurred. The reaction mixture was heated to 95 °C. After 30 h, the reaction mixture was cooled and analyzed using ^{1}H NMR spectroscopy: no H/D exchange in methane was apparent. 80% of platinum dication **5a** had been consumed. As before, several new platinum species were visible (Diagnostic methyl singlets at (^{1}H NMR 300 MHz, CF_3CD_2OD δ 1.91, 1.88, and 1.83 ppm).



Attempted C–H bond activation of cyclohexane using π-arene 8a. To a 0.700 mL of a 0.014 M solution of platinum dication **5a** in trifluoroethanol-d_3 was added 0.0050 mL of *p*-xylene (0.041 mmol). [The solution of **5a** was prepared by suspending 0.021 g of platinum dimethyl **1a** (0.031 mmol) in 2.05 mL of trifluoroethanol-d_3. To the resulting purple heterogeneous mixture was added 0.175 mL of a 0.477 M solution of BF_3 in trifluoroethanol-d_3. After brief agitation the mixture became a light orange solution. After 13 h, the orange solution had faded to light yellow.] The reaction progress (or lack thereof) was analyzed periodically using ^{1}H NMR spectroscopy. Initial analysis of the reaction revealed a 33:66 mixture of π-arene **8a** and dication **5a**. The mixture was saturated by adding 0.080 mL of cyclohexane (0.740 mmol). Analysis of the resulting mixture using ^{1}H NMR spectroscopy revealed no apparent change in the ration of **8a** and **5a**. The reaction mixture was heated to 50 °C. After 24 h, analysis using ^{1}H NMR spectroscopy revealed that the residual hydroxyl peak of solvent had increased by a factor of six. The integration of the peaks associated with *p*-xylene was diminished, whereas the cyclohexane peak (1.47 ppm) remained unchanged. The reaction mixture was heated to 95 °C.

After 8 h, analysis using ^{1}H NMR spectroscopy revealed that both **5a** and **8a** were consumed to form a variety of new complexes. As before, the integration of the cyclohexane peak was unchanged.

VII. References

(1) Brown, H. C.; Johannesen, R. B. *J. Am. Chem. Soc.* **1953**, *75*, 16-20.
(2) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366-6367.
(3) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378-1399.
(4) Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 15034-15035.
(5) Driver, T. G.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2005**, *24*, 3644-3654.
(6) For a detailed description and application of the specially designed high pressure NMR apparatus, see: Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2006**, *128*, 2005-2016.

*VIII. Crystallographic data of **14a***

Contents

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 614486.

Table 1. Crystal data and structure refinement

Empirical formula	$[C_{41}H_{57}N_2Pt]^+ [BF_4]^- \bullet CH_2Cl_2$
Formula weight	944.71
Crystallization Solvent	Dichloromethane/hexanes
Crystal Habit	Block
Crystal size	0.31 x 0.26 x 0.17 mm^3
Crystal color	Orange

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 31422 reflections used in lattice determination	2.49 to 38.30°
Unit cell dimensions	a = 16.2295(4) Å b = 14.5556(3) Å β= 113.1340(10)° c = 20.1968(5) Å
Volume	4387.44(18) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.430 Mg/m^3
F(000)	1912
Data collection program	Bruker SMART v5.630
θ range for data collection	1.78 to 42.85°

Completeness to $\theta = 42.85°$	93.9 %
Index ranges	$-29 \le h \le 28$, $-27 \le k \le 26$, $-38 \le l \le 38$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	121404
Independent reflections	30232 [R_{int}= 0.0637]
Absorption coefficient	3.367 mm^{-1}
Absorption correction	SADABS
Max. and min. transmission	1.000000 and 0.911896

Structure solution and Refinement

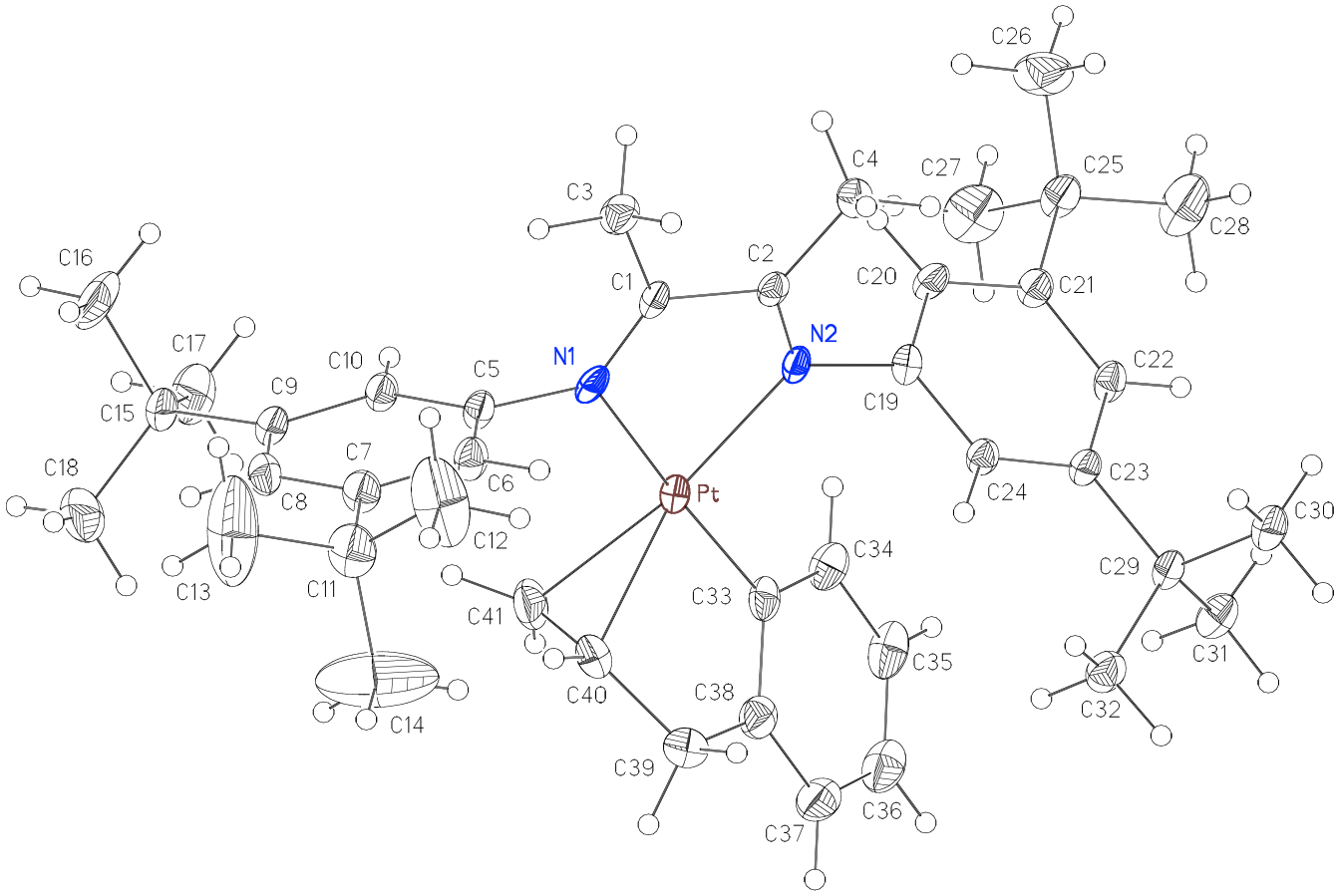
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	30232 / 0 / 483
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.429
Final R indices [I>2σ(I), 14960 reflections]	R1 = 0.0428, *w*R2 = 0.0733
R indices (all data)	R1 = 0.1167, *w*R2 = 0.0842
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Largest diff. peak and hole	5.713 and -2.940 e.$Å^{-3}$

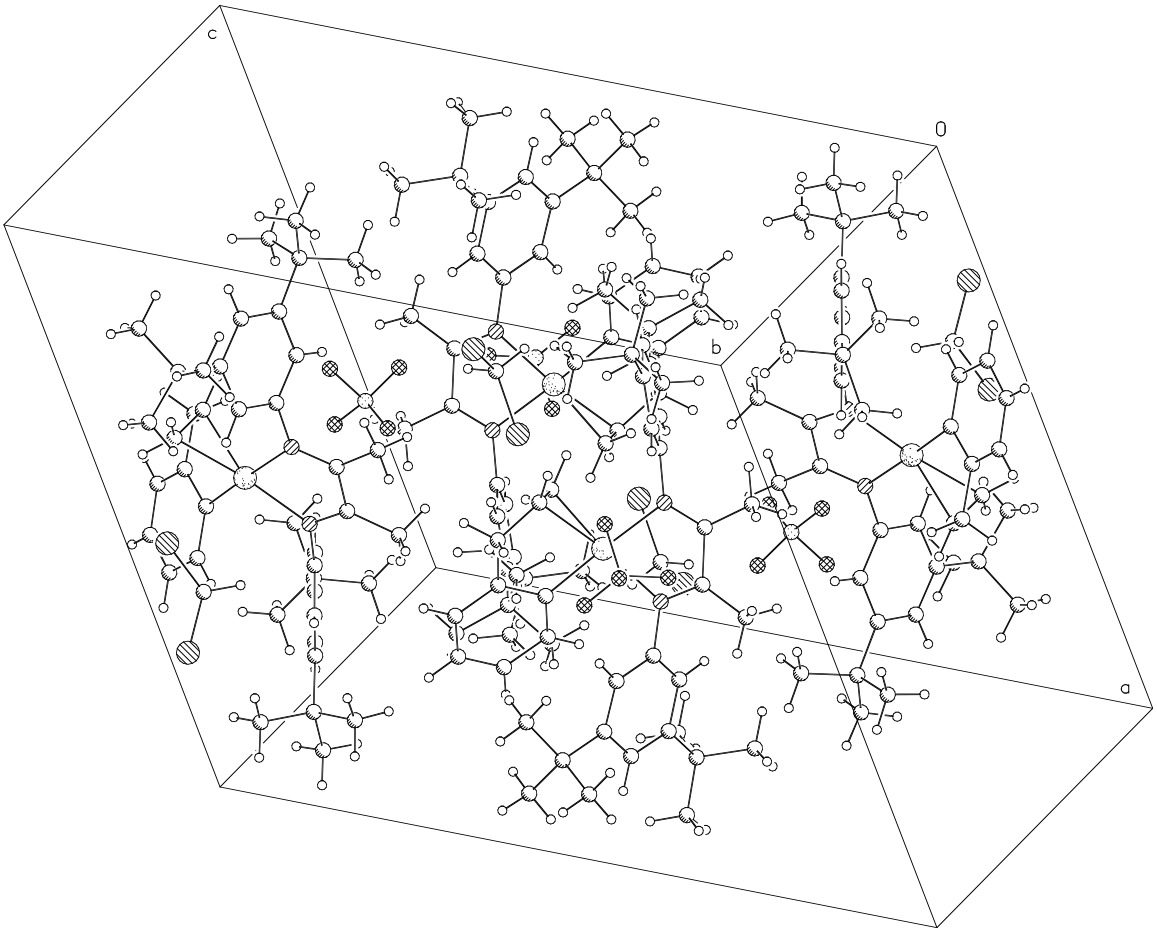
Special Refinement Details

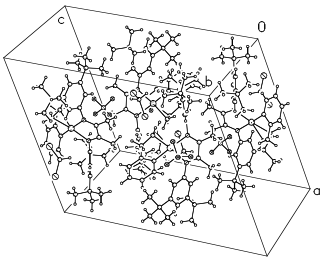
All difference Fourier peak greater than one electron lie very close to the Pt and could not be completely accounted for by absorption corrections. They represent no chemically reasonable alternatives and therefore it is assumed they arise from "noise".

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C26
C4
C27
C25
C28
C3
C2
C20
C21
C16
C1
N2
C22
C17
N1
C10
C5
C9
C19
C15
C7
C23
C18
C8
C6
Pt
C24
C30
C34
C12
C29
C13
C11
C33
C41
C35
C31
C40
C38
C32
C14
C39
C36
C37


c
0
b
a


c
0
a

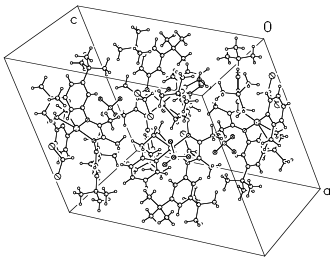

c
0
a

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pt	4776(1)	2512(1)	1033(1)	16(1)
N(1)	5719(1)	2166(1)	2069(1)	17(1)
N(2)	4057(1)	2668(1)	1669(1)	16(1)
C(1)	5451(2)	2273(1)	2584(1)	16(1)
C(2)	4491(1)	2574(2)	2352(1)	15(1)
C(3)	6002(2)	2134(2)	3366(1)	23(1)
C(4)	4127(2)	2768(2)	2906(1)	21(1)
C(5)	6631(2)	1925(2)	2204(1)	18(1)
C(6)	7299(2)	2578(2)	2489(1)	21(1)
C(7)	8178(2)	2371(2)	2574(1)	23(1)
C(8)	8334(2)	1504(2)	2351(2)	23(1)
C(9)	7666(2)	843(2)	2058(1)	21(1)
C(10)	6801(2)	1063(2)	1993(1)	19(1)
C(11)	8918(2)	3102(2)	2860(2)	33(1)
C(12)	8790(2)	3700(3)	3426(3)	64(1)
C(13)	9837(2)	2665(3)	3217(3)	83(2)
C(14)	8866(4)	3715(4)	2236(3)	101(2)
C(15)	7880(2)	-98(2)	1821(2)	24(1)
C(16)	8310(3)	-712(2)	2485(2)	44(1)
C(17)	7031(2)	-573(2)	1302(2)	37(1)
C(18)	8512(2)	7(2)	1433(2)	42(1)
C(19)	3134(2)	2956(2)	1375(1)	17(1)
C(20)	2468(2)	2353(1)	1354(1)	19(1)
C(21)	1567(2)	2615(2)	1012(1)	19(1)
C(22)	1383(2)	3485(2)	694(1)	19(1)
C(23)	2061(2)	4100(2)	708(1)	17(1)
C(24)	2941(2)	3822(2)	1061(1)	17(1)
C(25)	825(2)	1933(2)	974(2)	24(1)
C(26)	1018(2)	1538(2)	1725(2)	38(1)
C(27)	826(2)	1137(2)	472(2)	41(1)
C(28)	-100(2)	2374(2)	693(3)	53(1)
C(29)	1829(2)	5042(2)	342(1)	19(1)
C(30)	1605(2)	5703(2)	844(1)	24(1)
C(31)	1027(2)	4974(2)	-387(1)	26(1)
C(32)	2620(2)	5436(2)	193(2)	25(1)
C(33)	3864(2)	2939(2)	84(1)	20(1)
C(34)	2964(2)	2691(2)	-232(2)	25(1)
C(35)	2397(2)	3053(2)	-904(2)	30(1)
C(36)	2736(2)	3670(2)	-1254(2)	33(1)
C(37)	3630(2)	3909(2)	-954(2)	30(1)
C(38)	4197(2)	3543(2)	-294(1)	24(1)
C(39)	5179(2)	3778(2)	67(2)	29(1)
C(40)	5675(2)	3011(2)	565(2)	28(1)
C(41)	5497(2)	2078(2)	397(2)	32(1)
C(51)	6418(2)	5215(2)	4213(2)	42(1)
Cl(1)	5452(1)	4877(1)	4329(1)	42(1)
Cl(2)	7200(1)	4329(1)	4401(1)	78(1)

B(1)	5518(3)	4880(2)	2220(2)	44(1)
F(1)	6226(2)	4439(2)	2073(2)	85(1)
F(2)	5874(1)	5706(1)	2550(1)	44(1)
F(3)	5366(2)	4301(2)	2660(1)	99(1)
F(4)	4879(2)	5021(2)	1558(1)	56(1)

Table 3. Selected bond lengths [Å] and angles [°]

Pt-C(33)	2.006(2)	C(33)-Pt-N(2)	100.09(9)
Pt-N(2)	2.060(2)	C(33)-Pt-N(1)	175.22(8)
Pt-N(1)	2.111(2)	N(2)-Pt-N(1)	77.03(8)
Pt-C(41)	2.145(3)	C(33)-Pt-C(41)	83.72(11)
Pt-C(40)	2.151(3)	N(2)-Pt-C(41)	169.16(10)
		N(1)-Pt-C(41)	99.80(10)
		C(33)-Pt-C(40)	81.33(11)
		N(2)-Pt-C(40)	152.23(10)
		N(1)-Pt-C(40)	99.42(10)
		C(41)-Pt-C(40)	38.11(11)

Table 4. Bond lengths [Å] and angles [°]

Pt-C(33)	2.006(2)	B(1)-F(3)	1.316(4)
Pt-N(2)	2.060(2)	B(1)-F(4)	1.347(4)
Pt-N(1)	2.111(2)	B(1)-F(2)	1.386(4)
Pt-C(41)	2.145(3)	B(1)-F(1)	1.445(5)
Pt-C(40)	2.151(3)		
N(1)-C(1)	1.285(3)	C(33)-Pt-N(2)	100.09(9)
N(1)-C(5)	1.440(3)	C(33)-Pt-N(1)	175.22(8)
N(2)-C(2)	1.287(3)	N(2)-Pt-N(1)	77.03(8)
N(2)-C(19)	1.440(3)	C(33)-Pt-C(41)	83.72(11)
C(1)-C(3)	1.492(3)	N(2)-Pt-C(41)	169.16(10)
C(1)-C(2)	1.506(3)	N(1)-Pt-C(41)	99.80(10)
C(2)-C(4)	1.483(3)	C(33)-Pt-C(40)	81.33(11)
C(5)-C(6)	1.386(3)	N(2)-Pt-C(40)	152.23(10)
C(5)-C(10)	1.386(3)	N(1)-Pt-C(40)	99.42(10)
C(6)-C(7)	1.401(3)	C(41)-Pt-C(40)	38.11(11)
C(7)-C(8)	1.396(3)	C(1)-N(1)-C(5)	121.7(2)
C(7)-C(11)	1.537(4)	C(1)-N(1)-Pt	115.51(16)
C(8)-C(9)	1.395(4)	C(5)-N(1)-Pt	122.43(16)
C(9)-C(10)	1.396(3)	C(2)-N(2)-C(19)	121.0(2)
C(9)-C(15)	1.535(3)	C(2)-N(2)-Pt	116.83(16)
C(11)-C(13)	1.519(5)	C(19)-N(2)-Pt	121.86(15)
C(11)-C(14)	1.519(5)	N(1)-C(1)-C(3)	126.1(2)
C(11)-C(12)	1.514(5)	N(1)-C(1)-C(2)	114.9(2)
C(15)-C(18)	1.524(4)	C(3)-C(1)-C(2)	119.0(2)
C(15)-C(17)	1.530(4)	N(2)-C(2)-C(4)	125.2(2)
C(15)-C(16)	1.533(4)	N(2)-C(2)-C(1)	115.4(2)
C(19)-C(20)	1.379(3)	C(4)-C(2)-C(1)	119.4(2)
C(19)-C(24)	1.391(3)	C(6)-C(5)-C(10)	122.1(2)
C(20)-C(21)	1.403(3)	C(6)-C(5)-N(1)	119.3(2)
C(21)-C(22)	1.398(3)	C(10)-C(5)-N(1)	118.4(2)
C(21)-C(25)	1.540(3)	C(5)-C(6)-C(7)	119.7(2)
C(22)-C(23)	1.409(3)	C(8)-C(7)-C(6)	117.5(2)
C(23)-C(24)	1.383(3)	C(8)-C(7)-C(11)	122.2(2)
C(23)-C(29)	1.534(3)	C(6)-C(7)-C(11)	120.2(2)
C(25)-C(28)	1.522(4)	C(9)-C(8)-C(7)	123.4(2)
C(25)-C(26)	1.536(4)	C(8)-C(9)-C(10)	117.9(2)
C(25)-C(27)	1.538(4)	C(8)-C(9)-C(15)	120.9(2)
C(29)-C(31)	1.538(3)	C(10)-C(9)-C(15)	121.2(2)
C(29)-C(30)	1.541(3)	C(5)-C(10)-C(9)	119.5(2)
C(29)-C(32)	1.539(3)	C(13)-C(11)-C(14)	111.3(4)
C(33)-C(34)	1.393(4)	C(13)-C(11)-C(12)	106.4(3)
C(33)-C(38)	1.403(4)	C(14)-C(11)-C(12)	108.0(4)
C(34)-C(35)	1.409(4)	C(13)-C(11)-C(7)	111.4(3)
C(35)-C(36)	1.385(4)	C(14)-C(11)-C(7)	108.3(3)
C(36)-C(37)	1.379(4)	C(12)-C(11)-C(7)	111.3(3)
C(37)-C(38)	1.395(4)	C(18)-C(15)-C(17)	107.4(3)
C(38)-C(39)	1.509(4)	C(18)-C(15)-C(16)	109.9(3)
C(39)-C(40)	1.506(4)	C(17)-C(15)-C(16)	108.3(3)
C(40)-C(41)	1.402(4)	C(18)-C(15)-C(9)	110.6(2)
C(51)-Cl(1)	1.743(3)	C(17)-C(15)-C(9)	111.4(2)
C(51)-Cl(2)	1.744(4)	C(16)-C(15)-C(9)	109.2(2)

C(20)-C(19)-C(24)	122.0(2)
C(20)-C(19)-N(2)	120.2(2)
C(24)-C(19)-N(2)	117.6(2)
C(19)-C(20)-C(21)	119.6(2)
C(22)-C(21)-C(20)	117.8(2)
C(22)-C(21)-C(25)	122.6(2)
C(20)-C(21)-C(25)	119.6(2)
C(21)-C(22)-C(23)	122.8(2)
C(24)-C(23)-C(22)	117.7(2)
C(24)-C(23)-C(29)	121.2(2)
C(22)-C(23)-C(29)	121.1(2)
C(23)-C(24)-C(19)	120.1(2)
C(28)-C(25)-C(26)	108.3(3)
C(28)-C(25)-C(27)	109.1(3)
C(26)-C(25)-C(27)	108.5(2)
C(28)-C(25)-C(21)	112.6(2)
C(26)-C(25)-C(21)	109.8(2)
C(27)-C(25)-C(21)	108.4(2)
C(31)-C(29)-C(23)	111.0(2)
C(31)-C(29)-C(30)	109.9(2)
C(23)-C(29)-C(30)	108.5(2)
C(31)-C(29)-C(32)	107.2(2)
C(23)-C(29)-C(32)	111.2(2)
C(30)-C(29)-C(32)	109.1(2)
C(34)-C(33)-C(38)	118.2(2)
C(34)-C(33)-Pt	127.2(2)
C(38)-C(33)-Pt	114.60(19)
C(33)-C(34)-C(35)	120.9(3)
C(36)-C(35)-C(34)	119.6(3)
C(37)-C(36)-C(35)	120.0(3)
C(36)-C(37)-C(38)	120.6(3)
C(37)-C(38)-C(33)	120.6(3)
C(37)-C(38)-C(39)	123.4(3)
C(33)-C(38)-C(39)	116.0(2)
C(38)-C(39)-C(40)	109.9(2)
C(41)-C(40)-C(39)	123.4(3)
C(41)-C(40)-Pt	70.70(19)
C(39)-C(40)-Pt	105.47(19)
C(40)-C(41)-Pt	71.18(18)
Cl(1)-C(51)-Cl(2)	112.21(19)
F(3)-B(1)-F(4)	119.4(4)
F(3)-B(1)-F(2)	112.7(3)
F(4)-B(1)-F(2)	111.0(3)
F(3)-B(1)-F(1)	103.3(3)
F(4)-B(1)-F(1)	103.1(3)
F(2)-B(1)-F(1)	105.6(3)

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt	147(1)	144(1)	185(1)	-5(1)	55(1)	29(1)
N(1)	156(9)	83(7)	230(10)	31(7)	36(8)	5(6)
N(2)	139(8)	103(9)	219(9)	14(6)	62(7)	28(5)
C(1)	141(10)	113(9)	214(11)	22(7)	42(8)	24(6)
C(2)	159(9)	95(9)	203(9)	7(9)	66(7)	-1(8)
C(3)	197(12)	248(12)	226(13)	50(10)	53(10)	29(9)
C(4)	192(12)	226(11)	220(12)	15(8)	80(10)	28(8)
C(5)	142(10)	148(10)	232(12)	16(8)	55(9)	23(7)
C(6)	190(10)	145(11)	282(11)	-26(10)	85(8)	4(9)
C(7)	177(10)	196(14)	304(12)	1(9)	93(9)	-16(8)
C(8)	171(12)	234(12)	309(14)	32(10)	115(10)	42(9)
C(9)	233(12)	167(11)	238(12)	30(9)	99(10)	61(8)
C(10)	164(11)	144(10)	253(12)	8(8)	81(9)	11(8)
C(11)	199(13)	299(15)	460(18)	-35(13)	103(13)	-79(10)
C(12)	350(20)	540(20)	1000(40)	-440(20)	250(20)	-200(17)
C(13)	191(15)	590(30)	1480(50)	-430(30)	90(20)	-60(16)
C(14)	1110(50)	1070(40)	690(30)	100(30)	180(30)	-830(40)
C(15)	275(14)	184(11)	283(13)	13(10)	140(11)	81(9)
C(16)	690(30)	235(15)	374(18)	63(13)	187(17)	253(15)
C(17)	436(19)	245(14)	399(18)	-98(12)	132(15)	60(12)
C(18)	540(20)	310(16)	570(20)	-27(15)	382(19)	80(14)
C(19)	146(10)	153(10)	199(11)	-14(8)	47(9)	27(7)
C(20)	205(11)	127(12)	229(11)	33(7)	66(9)	11(7)
C(21)	154(9)	168(13)	235(10)	12(9)	57(8)	-4(8)
C(22)	133(10)	159(10)	256(12)	4(9)	49(9)	11(7)
C(23)	170(11)	127(9)	190(11)	2(8)	61(9)	13(7)
C(24)	147(10)	141(10)	213(11)	7(8)	63(9)	1(7)
C(25)	158(11)	186(11)	345(15)	48(10)	58(10)	-19(8)
C(26)	331(17)	364(17)	457(19)	75(14)	171(15)	-126(13)
C(27)	373(18)	311(16)	500(20)	-56(14)	100(16)	-133(13)
C(28)	190(13)	350(20)	1000(30)	229(19)	197(16)	-4(12)
C(29)	165(11)	147(10)	224(12)	18(8)	52(9)	29(8)
C(30)	248(13)	172(11)	290(14)	-4(9)	91(11)	36(9)
C(31)	230(13)	225(12)	256(13)	31(10)	31(10)	23(9)
C(32)	227(13)	188(12)	327(15)	38(10)	106(11)	0(9)
C(33)	211(12)	186(11)	195(12)	-44(9)	68(9)	53(9)
C(34)	248(13)	192(13)	251(12)	-23(8)	42(10)	21(8)
C(35)	279(14)	283(14)	251(14)	-68(11)	1(11)	75(11)
C(36)	390(17)	330(15)	196(13)	-11(11)	50(12)	120(12)
C(37)	442(18)	260(14)	201(13)	12(10)	141(12)	81(12)
C(38)	313(14)	224(12)	207(12)	-11(9)	114(11)	63(10)
C(39)	319(16)	319(15)	284(14)	55(11)	162(12)	35(11)
C(40)	231(14)	332(16)	329(16)	41(12)	169(12)	68(11)
C(41)	334(17)	366(16)	292(16)	-5(13)	172(14)	148(13)
C(51)	580(20)	376(18)	365(18)	-76(14)	241(17)	-161(15)
Cl(1)	459(5)	439(5)	388(4)	39(4)	191(4)	-4(4)
Cl(2)	429(6)	849(9)	986(10)	-442(8)	183(6)	-11(5)

B(1)	720(30)	180(15)	340(20)	-10(13)	110(20)	-52(16)
F(1)	1000(20)	609(17)	960(20)	165(15)	407(18)	457(16)
F(2)	742(15)	164(8)	412(11)	-43(7)	233(10)	-123(8)
F(3)	1990(30)	565(15)	463(14)	-174(12)	543(18)	-832(19)
F(4)	440(13)	704(16)	467(13)	65(11)	98(10)	-186(11)